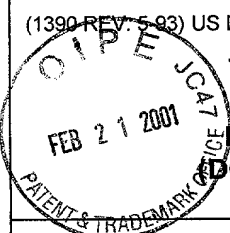


(1390 REV. 5-93) US DEPT. OF COMMERCE PATENT & TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER 108669
 <p align="center">TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371</p>		U.S. APPLICATION NO. (if known, sec 37 C.F.R.1.5) 09/763294
INTERNATIONAL APPLICATION NO. PCT/JP99/04575	INTERNATIONAL FILING DATE August 25, 1999	PRIORITY DATE CLAIMED August 26, 1998
TITLE OF INVENTION A LIQUID CRYSTAL ALIGNMENT AGENT AND LIQUID CRYSTAL DEVICE USING THE LIQUID CRYSTAL ALIGNMENT AND METHOD FOR ALIGNMENT OF LIQUID CRYSTAL MOLECULES		
APPLICANTS FOR DO/EO/US Yukihiro MIYAMA, Takayasu NIHIRA, Hideyuki ENDO, Hiroyoshi FUKURO, Yu NAGASE, Eiichi AKIYAMA and Nobukatsu NEMOTO		
<p>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). <input checked="" type="checkbox"/> has been transmitted by the International Bureau. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US) <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> have been transmitted by the International Bureau. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input checked="" type="checkbox"/> An oath or declaration of the inventors (35 U.S.C. 371(c)(4)). <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)). <p>Items 11. to 16. below concern other document(s) or information included:</p> <ol style="list-style-type: none"> <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> Entitlement to small entity status is hereby asserted. <input type="checkbox"/> Other items or information: 		

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/763294	INTERNATIONAL APPLICATION NO. PCT/JP99/04575	ATTORNEY'S DOCKET NUMBER 108669
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17. <input checked="" type="checkbox"/> The following fees are submitted: Basic National fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO \$860.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) \$690.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$710.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1,000.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$ 100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =	CALCULATIONS	PTO USE ONLY																
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	\$																	
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%;">Claims</th> <th style="width: 20%;">Number Filed</th> <th style="width: 10%;">Number Extra</th> <th style="width: 10%;">Rate</th> </tr> <tr> <td>Total Claims</td> <td>15 - 20 =</td> <td>0</td> <td>X \$ 18.00</td> </tr> <tr> <td>Independent Claims</td> <td>1 - 3 =</td> <td>0</td> <td>X \$ 80.00</td> </tr> <tr> <td colspan="3">Multiple dependent claim(s) (if applicable)</td> <td>+ \$270.00</td> </tr> </table>	Claims	Number Filed	Number Extra	Rate	Total Claims	15 - 20 =	0	X \$ 18.00	Independent Claims	1 - 3 =	0	X \$ 80.00	Multiple dependent claim(s) (if applicable)			+ \$270.00	\$	
Claims	Number Filed	Number Extra	Rate															
Total Claims	15 - 20 =	0	X \$ 18.00															
Independent Claims	1 - 3 =	0	X \$ 80.00															
Multiple dependent claim(s) (if applicable)			+ \$270.00															
TOTAL OF ABOVE CALCULATIONS =	\$860.00																	
Reduction by 1/2 for filing by small entity, if applicable.	-																	
SUBTOTAL =	\$																	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 month from the earliest claimed priority date (37 CFR 1.492(f)).	+																	
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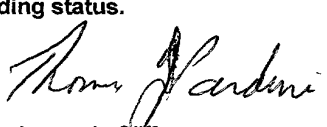
a. ☒ Check No. 116445 in the amount of \$860 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of \$_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Director is hereby authorized to charge any additional fees which may be required, or credit any overpayment, to Deposit Account No. 15-0461. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:
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 P.O. Box 19928
 Alexandria, Virginia 22320


 NAME: James A. Oliff
 REGISTRATION NUMBER: 27075

 NAME: Thomas J. Pardini
 REGISTRATION NUMBER: 30,411

09/763294

JC02 Rec'd PCT/PTO 21 FEB 2001

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Yukihiro MIYAMA, Takayasu NIHIRA, Hideyuki
ENDO, Hiroyoshi FUKURO, Yu NAGASE, Eiichi
AKIYAMA and Nobukatsu NEMOTO

Application No.: U.S. National Stage of
PCT/JP99/04575

Filed: February 21, 2001

Docket No.: 108669

For: A LIQUID CRYSTAL ALIGNMENT AGENT AND LIQUID CRYSTAL DEVICE
USING THE LIQUID CRYSTAL ALIGNMENT AND METHOD FOR ALIGNMENT
OF LIQUID CRYSTAL MOLECULES

PRELIMINARY AMENDMENT

Director of the U.S. Patent and Trademark Office
Washington, D. C. 20231

Sir:

Prior to initial examination, please amend the above-identified application as follows:

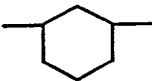
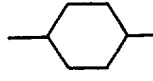
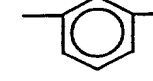
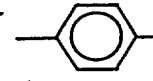
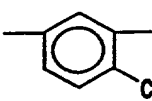
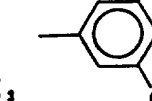
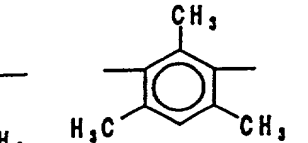
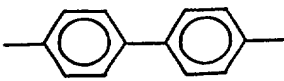
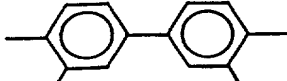
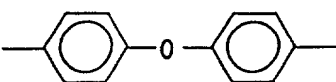
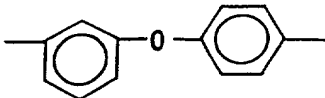
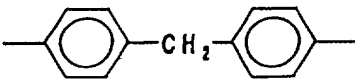
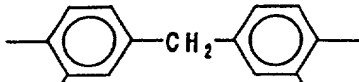
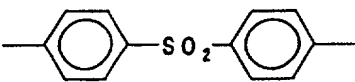
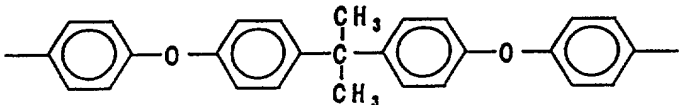
IN THE CLAIMS:

Please replace claims 3, 5, 6, 8-10, 12, 14, 15 as follows:

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[illegible]

-- **Claim 5.** (Amended)

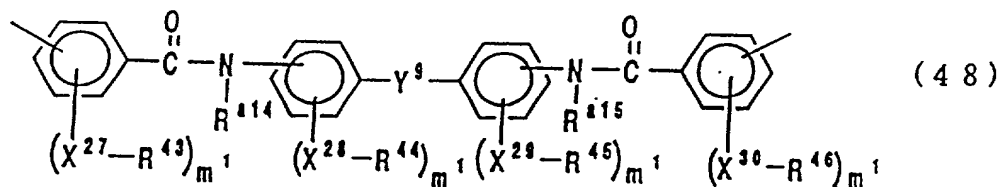
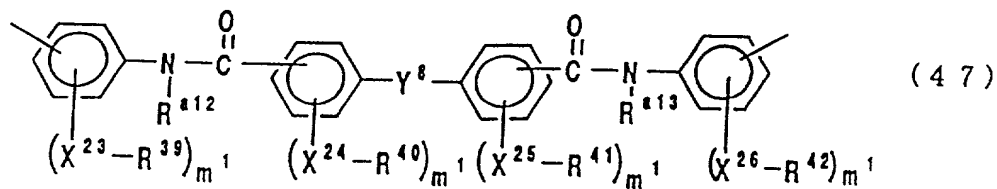
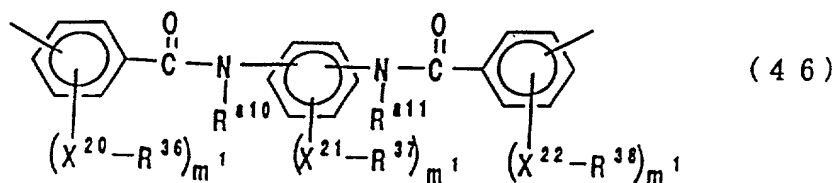
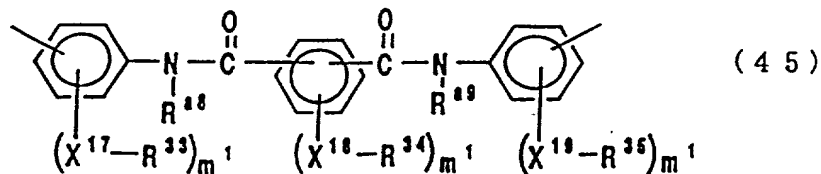
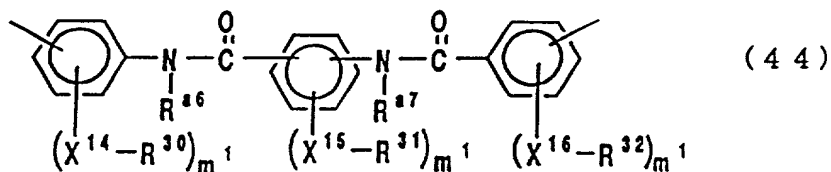
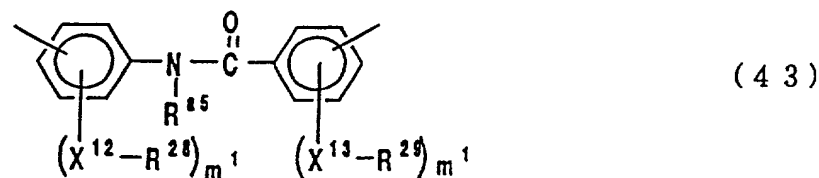
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-- Claim 6. (Amended)

Liquid crystal alignment agent according to Claim 1, where said polymer compound is polyimide precursor or polyimide obtained by chemical or heat imidization of said polyimide precursor.--

-- Claim 8. (Amended)

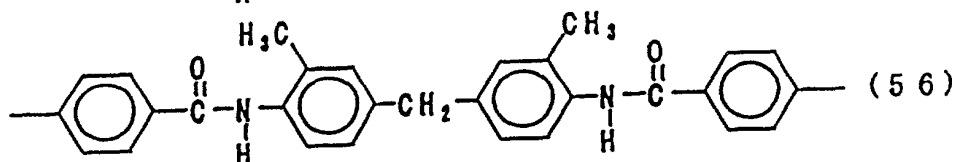
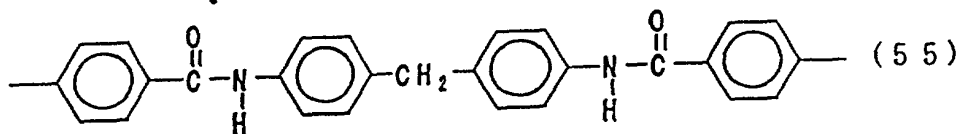
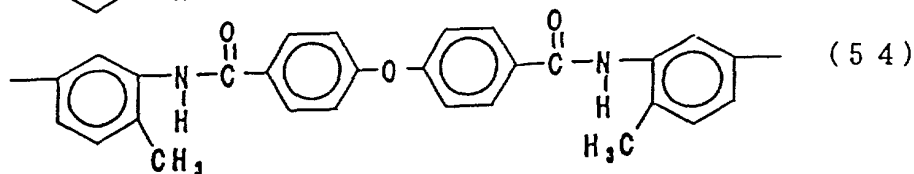
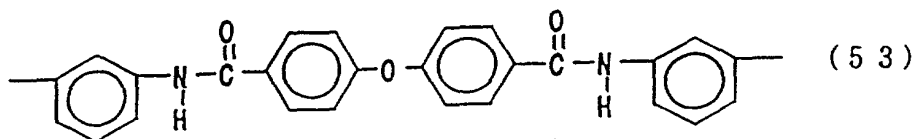
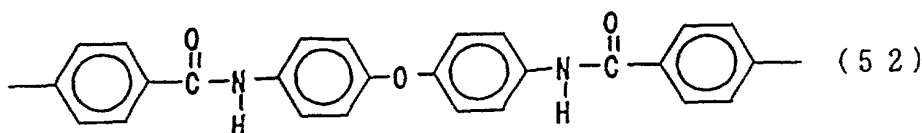
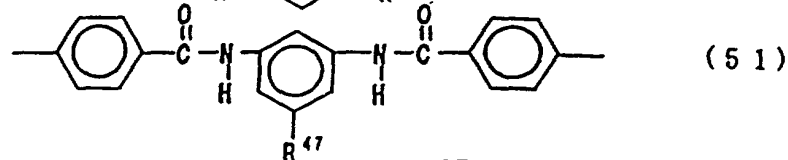
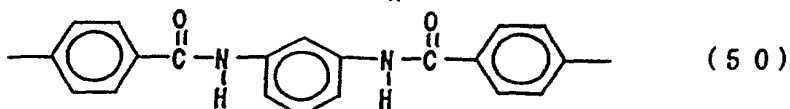
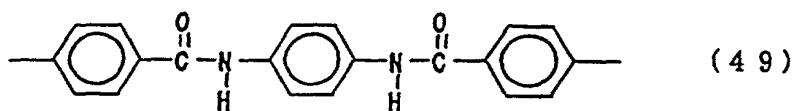
Liquid crystal alignment agent according to Claim 6, where R^{27} in the general formula (42a) and (42b) above is selected from the general formula (43) – (48) below



wherein $X^{12} - X^{30}$ are independently of each other single bond, O, CO_2 , OCO or CH_2O ; $R^{28} - R^{46}$ are independently of each other hydrogen, halogen, C_1-C_{24} alkyl, C_1-C_{24} alkyl containing fluorine, aryl, propargyl, phenyl or substituted phenyl; $R^{a5} - R^{a15}$ are independently of each other hydrogen, alkyl, substituted alkyl, aryl or propargyl; Y^8 and Y^9 are O, S, SO_2 , CH_2 , NH, NHCO or CONH, and m^1 is an integer of 1 - 4 with the proviso that $R^{28} - R^{46}$ are hydrogen or halogen, then $X^{12} - X^{30}$ are single bond. --

-- Claim 9. (Amended)

Liquid crystal alignment agent according to Claim 6
, where radical for R^{27} in the general formula (42a) and (42b) above is selected from in the formula (49) - (56) below



wherein R^{47} is halogen, C_1-C_{24} alkyl, C_1-C_{24} alkoxy or C_1-C_{24} alkoxycarbonyl. --

-- Claim 10. (Amended)

Liquid crystal alignment agent according to Claim 1, where said polymer compound is polyurethane. --

-- Claim 12. (Amended)

Liquid crystal alignment agent according to Claim 1, where said polymer compound is polyurea. --

-- Claim 14. (Amended)

Liquid crystal device by the use of the liquid crystal alignment agent according to Claim 1. --

-- Claim 15. (Amended)

Alignment method of liquid crystals characterized by the use of the liquid crystal alignment agent according to Claim 1, where light or electron rays being irradiated over the thin polymer film formed on the surface of the substrate and achieving liquid crystal alignment without rubbing action. --

REMARKS

Claims 1-15 are pending. Claims 3, 5, 6, 8-10, 12, 14, 15 are amended to eliminate multiple dependencies. Prompt and favorable consideration on the merits is respectfully requested.

Respectfully submitted,



James A. Oliff
Registration No. 27,075

Thomas J. Pardini
Registration No. 30,411

JAO:TJP/kaf

Enclosure:
Appendix

Date: February 21, 2001

OLIFF & BERRIDGE, PLC
P.O. Box 19928
Alexandria, Virginia 22320
Telephone: (703) 836-6400

DEPOSIT ACCOUNT USE AUTHORIZATION Please grant any extension necessary for entry; Charge any fee due to our Deposit Account No. 15-0461
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Description

A liquid crystal alignment agent and liquid crystal device using the liquid crystal alignment, and method for alignment of liquid crystal molecules

Technical Field

The present invention relates to a liquid crystal alignment agent and liquid crystal device by the use of the liquid crystal alignment agent thereof, and in more detail relates to a novel liquid crystal alignment agent used in the method of aligning liquid crystal molecules by irradiating light over the surface of a thin film of polymer without rubbing treatment, and the liquid crystal device and liquid crystal molecules by the use of liquid crystal alignment agent having polymer with the specific unit structure in manifesting their high sensitivity as well as their high heat stability and high light resistance in regard to the alignment of liquid crystal molecules in comparison to the pertinent art in existence described above..

Background Art

Liquid crystal display devices are display devices utilizing electrooptical changes of liquid crystal, and an attention has been drawn to their features such that the devices are small in size and light in weight, and power consumption is small. Accordingly, in recent years, they have undergone remarkable developments as display devices for various displays. Among them, an electric field effect type (TN type) is representative wherein nematic liquid crystal having a positive dielectric anisotropy, is used, liquid crystal molecules are aligned in parallel with substrates at the respective interfaces of a pair of mutually opposing electrode substrates, and the two substrates are combined so that the alignment directions of liquid crystal molecules will cross each other.

With such a TN type liquid crystal display device, it is important to align long axial directions of liquid crystal molecules uniformly in parallel with the substrate surface and to align liquid crystal molecules with a constant tilt

alignment angle (hereinafter referred to as a pre-tilt angle) to the substrate.

As typical methods for aligning liquid crystal molecules in such a manner, two methods have heretofore been known. The first method is a method wherein an inorganic substance such as silicon oxide is vapor-deposited from an oblique direction to the substrate to form an inorganic film on the substrate, so that the liquid crystal molecules will be aligned in the direction of vapor-deposition. This method is not industrially efficient, although constant alignment with a predetermined tilt angle can be obtained.

The second method is a method wherein an organic coating film is formed on the substrate surface, and the film surface is rubbed in a predetermined direction with a cloth of e.g. nylon or polyester so that liquid crystal molecules are aligned in the rubbing direction. An organic coating film (called liquid crystal alignment film or alignment film) is usually formed by coating the liquid crystal alignment agent over the surface of a substrate. By this method, constant alignment can be obtained relatively easily, and this method is industrially most commonly employed. As the organic film, polyvinyl alcohol, polyoxyethylene, polyamide or polyimide may, for example, be mentioned. However, polyimide is most commonly employed from the viewpoint of the mechanical strength, chemical stability, thermal stability, etc. As typical examples of polyimide used for such liquid crystal alignment films, those disclosed in JP-A 61-47932 may be mentioned.

The treating method for liquid crystal alignment by rubbing polyimide film is an industrially useful method which is simple and excellent in productivity. However, as the demands for high precision and high performance of liquid crystal display devices have increased and new display systems corresponding to such demands have been developed, various problems of the rubbing method have been pointed out. For example, a STN (Super Twisted Nematic) system wherein the twist angle of a TN type liquid crystal display is increased, an AM (Active Matrix) system wherein switching elements are formed for individual electrodes, and a FLC (ferroelectric) or AFLC (antiferroelectric) system wherein ferroelectric liquid crystal or antiferroelectric liquid crystal is employed, may be mentioned as such examples. In the STN system, contrast is high, and scratches on the alignment film surface formed by rubbing, become display

response and uniform alignment of smectic liquid crystal only by simple rubbing treatment. In the AM system, the mechanical force or static electricity due to rubbing is likely to destroy the switching elements, and dusting by rubbing tends to lead to display defects. Since AM system in particular drives liquid crystals with semiconductor devices such as TFT (thin film transistor) and basically requires absolute cleanability in its semiconductor technology, the process such as rubbing is not strictly speaking the best method in practical industrial production.

For the purpose of solving such problems, a so-called "rubbing-less" alignment method wherein liquid crystal is aligned without rubbing, has been studied, and various methods have been proposed. For example, a method wherein photochromic molecules are introduced to the alignment film surface, so that molecules on the alignment film surface are aligned by light (JP-A-4-2844), a method wherein molecular chains constituting an alignment film, are aligned by means of a LB film (Langmuir-Blodgett film) (S. Kobayashi et al, Jpn. J. Appl. Phys., 27, 475 (1988)) and a method wherein an alignment film is press-bonded on a preliminarily alignment-treated substrate to transfer the alignment (JP-A-6-43458), have been studied. However, when the industrial productivity is taken into account, they can not be said to be useful as substitutes for the rubbing method.

Whereas, various methods have been proposed wherein periodical irregularities are artificially formed on the alignment film surface, and liquid crystal molecules are aligned along such irregularities. The most simple method of this type is a method wherein a replica having periodical irregularities is preliminarily prepared, and a thermoplastic film is heated and pressed thereon to transfer the irregularities onto the film (JP-A-4-172320, JP-A-4-296820, JP-A-4-311926 etc.). By this method, it is certainly possible to prepare a film having periodical irregularities on its surface efficiently, but it has been impossible to obtain practical reliability as high as a polyimide film used in the rubbing method. Whereas, a method has been proposed in which a light with high energy, such as electron rays (JP-A-4-97139), α -rays (JP-A-2-19836), X-rays (JP-A-2-2515) or excimer laser (JP-A-5-53513), is applied to a polyimide film having high reliability to form periodical irregularities on the film surface. However, to use a light source for such high energy, can not hardly be said to be an efficient

treating method for alignment when an industrial production where alignment treatment is continuously carried out uniformly over the entire surface of a large size substrate, is taken into consideration.

On the other hand, as an efficient method for forming periodical irregularities on the surface of a polyimide film having high reliability, a photolithographic method may be mentioned. The polyimide is used as an insulating film for semiconductors by virtue of its high insulating property and excellent electric characteristics, and in recent years, a so-called photosensitive polyimide has been developed which is a polyimide having a photocurable nature by itself. There has been an attempt to form a periodical irregularities by a photolithographic method using this photocurable polyimide. By this method, irregularities have certainly been formed on the surface of the polyimide film, but since the photocurable polyimide was initially developed as an insulating film, the properties to align liquid crystal have been inadequate. Further, it has been necessary to apply a buffer coating layer (JP-A-4-245224), and consequently, the process has been complex and can not be regarded as an efficient treating method for alignment which can be a substitute for the rubbing method when the industrial productivity is taken into consideration.

As a new treating method for alignment which has recently been found, a method has been proposed in which polarized ultraviolet rays, etc. are applied to a polymer film surface to align liquid crystal molecules without carrying out rubbing treatment. The following reports are available as such examples.

W. M. Gibbons *et al.*, Nature, 351, 49 (1991), Y. Kawanishi *et al.*, Mol. Cryst. Liq. Cryst., 218, 153 (1992), M. Shadt *et al.*, Jpn. J. Appl. Phys. 31, 2155 (1992), and Y. Iimura *et al.*, Jpn. J. Appl. Phys. 32, L93 (1993).

These methods are characterized in that liquid crystal is aligned in a predetermined direction by irradiation of polarized light without requiring conventional rubbing treatment. These methods have merits such that they are free from problems such as static electricity and scratches on the film surface by the rubbing method, and the process is simple when industrial production is taken into consideration.

Namely, the liquid crystal alignment method using irradiation of polarized light proposed here is considered to be an attractive method as a new treatment method for liquid crystal alignment without requiring rubbing treatment, although it is still in a fundamental research stage.

The use of polymer compounds with light reacting radicals at the side chain of polymer molecules as the raw materials in aligning liquid crystal film has been proposed in the reports hitherto because of the necessity in getting photochemical sensitivity against polarized light. Polyvinyl cinnamate may be a typical example of such material and cinnamate as such manifests anisotropy by dimerizing at the side chain initiated by light irradiation leading to aligning liquid crystals in this case. In other embodiment reported, aligning liquid crystal molecules in a certain direction can be achieved by irradiating polarized light over the film surface in which low molecular weight dichroism azo dyestuff are dispersed into polymer materials. Further, the possibility of the alignment of liquid crystal molecules by the irradiation with polarized ultraviolet rays and the like over the specific polyimide film has been reported. In this instance, the alignment of liquid crystals may be manifested by the decomposition of main chain of polyimides in a defined direction.

Polymer material system with light reacting radical introduced to the side chain of polymer exemplified by polyvinyl cinnamate do not show sufficient heat resistance against the alignment, and thus is not fully reliable in practical aspect of production yet. In regard to the dispersion of low molecular weight dichroism dyestuff, stability against heat and light is a problem awaiting solution for dispersion system in view of practical aspect as dyestuff which align liquid crystals are themselves of low molecular weight. In addition, although polyimides themselves show high reliability for heat resistance in the method of irradiating polarized ultraviolet rays on specific polyimides, the real possibility of not getting full dependability for the future practical use still exists as its alignment mechanism is thought to be resulting from the decomposition with light. Moreover, decreased productivity can be expected due to high energy for light irradiation required for satisfactory alignment of liquid crystals.

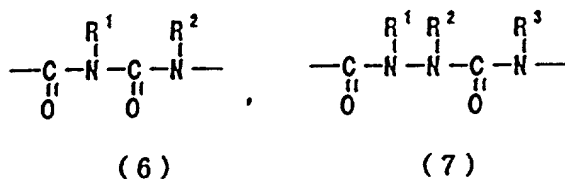
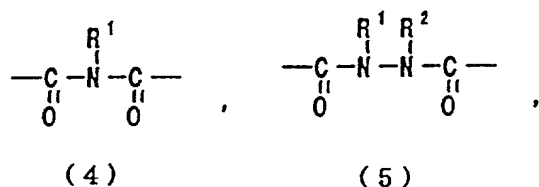
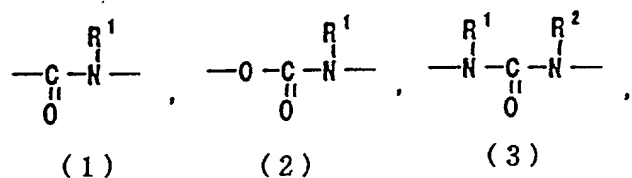
In these respects, materials proposed heretofore for liquid crystal alignment with the irradiation of light are not satisfactory in regard to their

alignment with the irradiation of light are not satisfactory in regard to their alignment strength and stability in addition to their sensitivity, and therefore practical use of rubbing-less alignment with light irradiation is an important issue to be considered at present.

Disclosure of Invention

The object of the present invention relates to the liquid crystal alignment agent which can align liquid crystals without rubbing treatment of the liquid crystal alignment film by the light irradiation over the liquid crystal alignment film, and also relates to the liquid crystal alignment agent of polymer material system with the specific unit structure with which uniform and stable alignment of liquid crystals can be effectively achieved with their high heat stability and high light resistance in regard to the alignment attained.

Inventors finally accomplished the present invention as a result of their eager effort to solve problems described above. That is to say that the present invention relates to the liquid crystal alignment agent which form the liquid crystal alignment film comprising of a thin alignment film over the substrate where irradiation of light or electron rays align liquid crystal molecules without any rubbing treatment, and said liquid crystal alignment agent comprises of polymer compound having bonds shown in the general formula (1) – (7) below



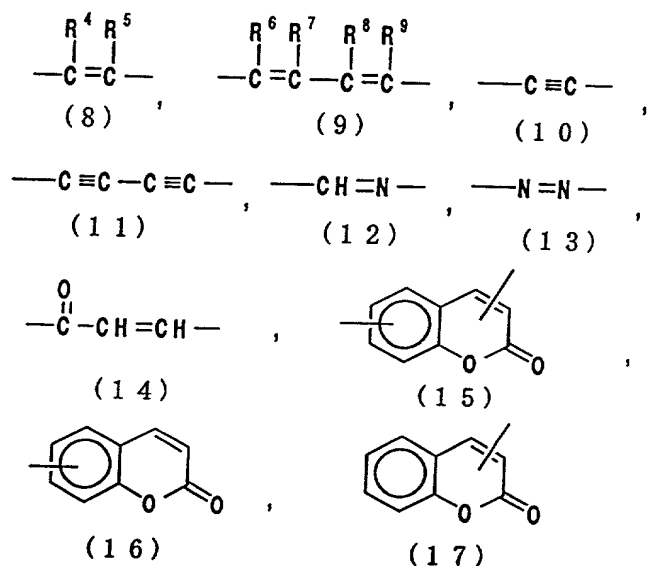
wherein R^1 , R^2 and R^3 are independently of each other hydrogen, alkyl, substituted alkyl, aryl or propagyl in the main chain of polymer compound with number average molecular weight of 1,000 – 300,000, and said bond makes the direct bond with either divalent or trivalent aromatic group at the both ends of said bond or with divalent or trivalent aromatic group making the direct bond at one end while at the other forming the direct bond with divalent or trivalent alicyclic hydrocarbon group, and liquid crystal elements by the use of said liquid crystal alignment agent and also the method of aligning liquid crystals by the use of said liquid crystal alignment agent.

As stated above, not only an initial alignment of liquid crystals alone but also more effective and stable alignment are necessary in order for the practical application of aligning liquid crystals by the irradiation of polarized light from the standpoint of reliability and productivity. In preparing practical industrial application, the selection of polymer structure having high heat and light stability as well as finding the liquid crystal alignment agent from polymer material system with broader selection latitude are desirable.

The liquid crystal alignment agent in the present invention relates to the thin polymer film coated and formed on said electrode substrate such as glass or plastic film so as to align liquid crystals and to control pre-tilt angle. Namely, the liquid crystal alignment agent in the present invention is applied and cured to a transparent substrate such as a transparent glass or plastic film as combined with a transparent electrode so as to form the thin polymer film, and then irradiating light or electron rays over the film in order to produce the liquid crystal alignment film without the necessity of rubbing treatment. The liquid crystal alignment agent in the present invention is under the normal circumstances used in the form of solution.

The thin polymer film formed with liquid crystal alignment agent of the present invention in which having structural characteristics of at least one bond shown in the general formula (1) - (7) in the main chain of the polymer compound forming said thin polymer film, and divalent or trivalent aromatic group forming the direct bond at the both ends of the said bond, or either divalent or trivalent aromatic group making the direct bond at one end while at the other forming the direct bond with divalent or trivalent alicyclic hydrocarbon

group so as to achieve effective and uniform as well as stable liquid crystal alignment with the irradiation with light or electron rays is important in order to achieve the object of the present invention. It is also preferred to have 20 to 100 mole % of the unit structure of the polymer in the structure for the effective liquid crystal alignment. Aromatic or alicyclic group described above can have substituting group. It is also preferred that glass transition point of polymer should be 200°C or higher in order to obtain heat stability of alignment. At the same time, the thin polymer film formed on the substrate can chemically change with the irradiation of light and the resulting reaction product can have the glass transition point of 200°C or higher. Radicals which induce dimerization reaction or isomerization reaction such as radicals shown in the general formula of (8) – (17)



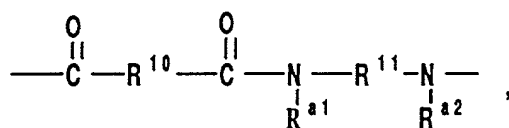
wherein R^4 , R^5 , R^6 , R^7 , R^8 and R^9 are independently of each other hydrogen, halogen, alkyl, substituted alkyl, substituted alkoxy, carboxyl, alkoxy carbonyl or cyano group; are not necessary needed.

Preferred example of alkyl group of substituting radicals shown in the general formula of (1) - (7) described above can be lower alcohol such as methyl, ethyl, propyl, i-propyl, butyl, i-butyl, s-propyl and t-butyl in addition to generally used long chain alkyl having up to 24 carbon atoms. Also preferred example of substituted alkyl is such as trifluoromethyl, 2,2,2-trifluoroethyl, perfluoroethyl, 3,3,3-trifluoropropyl, perfluoropropyl, hexafluoro-i-propyl, 3,3,4,4,4-

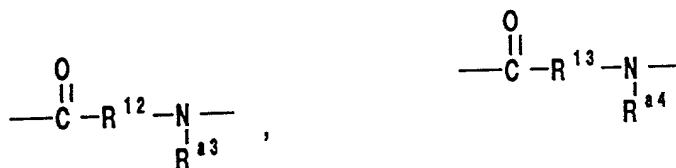
pentafluorobutyl and perfluorobutyl of lower alkyl groups containing fluorine, generally used fluorine containing long chain alkyl of up to about 24 carbon atoms, and benzyl and benzyl substituted with halogen, alkyl, alkoxy or alkoxycarbonyl on the benzene ring.

There is no limitation for the polymer compound of the present invention as long as the polymer compound have structural characteristics of at least one bond shown above in the general formulas (1) - (7), and divalent or trivalent aromatic groups forming the direct bond at the both ends of said bond, or either divalent or trivalent aromatic group making the direct bond at one end while at the other forming the direct bond with divalent or trivalent alicyclic hydrocarbon, but polyamide, polyurethane, polyurea or polyimide precursor having any one of the bond described above in the general formula of (1) - (7) or polyimide obtained by chemical or heat imidation of polyimide precursor are preferred from the view point described above.

Preferred example of polymer compounds are polyimide with divalent organic radicals shown in the general formula (18) or the formula (19a) and (19b)



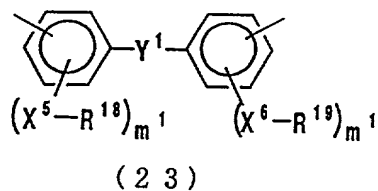
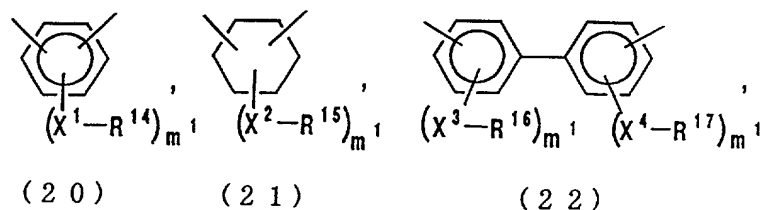
(18)



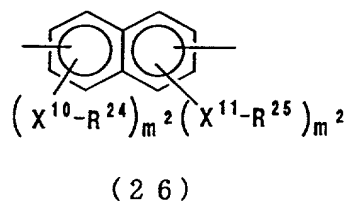
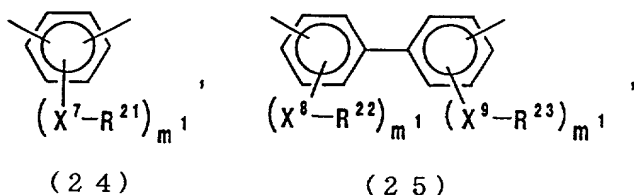
(19a)

(19b)

wherein R¹⁰, R¹¹, R¹² and R¹³ are of general formulas (20) - (23)



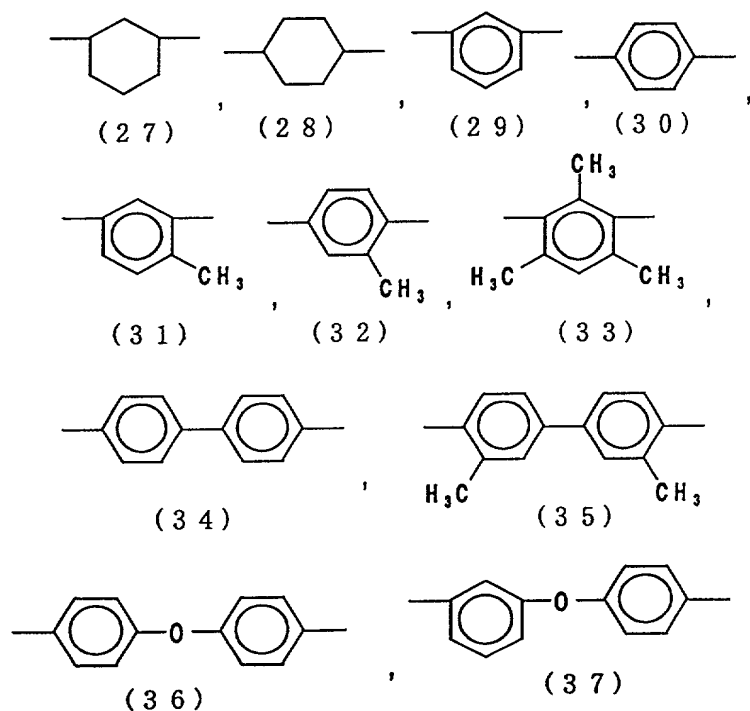
wherein X^1 , X^2 , X^3 , X^4 , X^5 and X^6 are independently of each other single bond, O, CO₂, OCO, CH₂O, NHCO or CONH; R^{14} , R^{15} , R^{16} , R^{17} , R^{18} and R^{19} are independently of each other hydrogen, halogen, C₁-C₂₄ alkyl, C₁-C₂₄ alkyl containing fluorine, aryl, propargyl, phenyl or substituted phenyl; Y^1 are O, S, CO, CO₂, SO₂, CH₂, NH, NHCO, Y^2 -Ar¹-Y³, Y^4 -(CH₂)^{n¹}-Y⁵ or Y^6 -Ar²-R²⁰-Ar³-Y⁷; Y^2 , Y^3 , Y^4 , Y^5 , Y^6 and Y^7 are independently of each other O, S, CO, CO₂, SO₂, CH₂, NH or NHCO; n^1 is an integer of 1 to 10; R²⁰ is C₁-C₅ straight or branched lower alkylene, fluoroalkylene or alkylenedioxy, and further Ar¹, Ar² and Ar³ are independently of each other in the general formulas (24), (25) or (26)

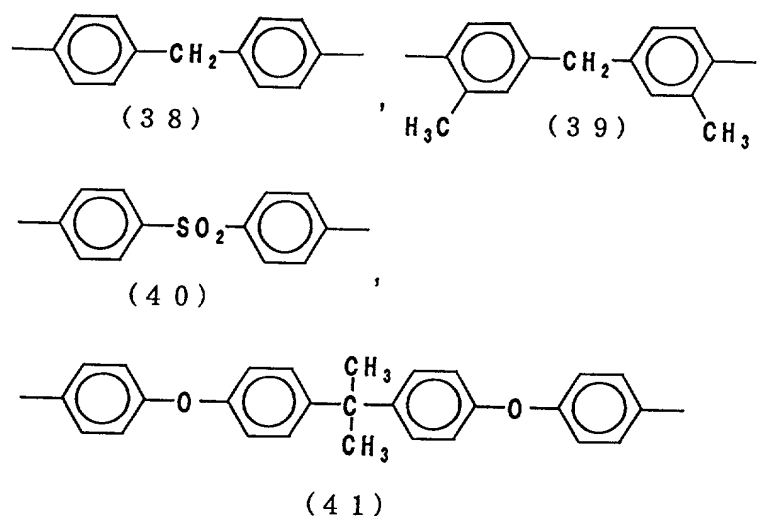


wherein X^7 , X^8 , X^9 , X^{10} and X^{11} are independently of each other single bond, O,

CO₂, OCO, CH₂O, NHCO or CONH; R²¹, R²², R²³, R²⁴ and R²⁵ are independently of each other hydrogen, halogen, C₁-C₂₄ alkyl, C₁-C₂₄ alkyl containing fluorine, aryl, propargyl, phenyl or substituted phenyl; m¹ is an integer of 1 - 4 and m² is an integer of 1 - 3, but with the proviso that R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²¹, R²², R²³, R²⁴ and R²⁵ are hydrogen or halogen, then X¹, X², X³, X⁴, X⁵, X⁶, X⁷, X⁸, X⁹, X¹⁰ and X¹¹ are single bond, and Ra¹, Ra², Ra³ and Ra⁴ are independently of each other hydrogen, alkyl, substituted alkyl, aryl or propargyl.

Further, when practicality and generality are considered, R¹⁰ and R¹¹ in the general formula (18) described above, or R¹² and R¹³ in the general formula (19a) and (19b) are independently of each other selected from in the general formula (27) - (41) described below





$\text{C}_1\text{—C}_{24}$ alkyl group of R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{21} , R^{22} , R^{23} , R^{24} and R^{25} in the general formula of (20) - (26) described above can be lower alkyl group such as methyl, ethyl, propyl, i-propyl, butyl, i-butyl, s-butyl or t-butyl, and additionally generally used long chain alkyl, and alkyl group containing alicyclic hydrocarbon group such as cyclohexyl and bicyclohexyl. Fluorine containing $\text{C}_1\text{—C}_{24}$ alkyl group includes fluorine containing lower alkyl such as trifluoromethyl, 2,2,2-trifluoroethyl, perfluoroethyl, 3,3,3-trifluoropropyl, perfluoropropyl, hexafluoro-i-propyl, 3,3,4,4,4-pentafluorobutyl and perfluorobutyl, and additionally generally used long chain alkyl containing fluorine.

Substituting groups in substituted phenyl radical are for example halogen, alkyl, alkyl containing fluorine, alkoxy, alkoxy containing fluorine, alkoxycarbonyl or alkoxycarbonyl containing fluorine.

Radicals of R^{a1} , R^{a2} , R^{a3} and R^{a4} in general formula described above are the same as radical of R^1 in the general formula (1). Polyamide described above with radicals R^{a1} , R^{a2} , R^{a3} and R^{a4} other than hydrogen can be obtained by the methods described below.

They can be obtained by introducing desired radicals with preferred ratio by the use of known polymer reaction at N of amide radical of polyamide in which R^{a1} , R^{a2} , R^{a3} and R^{a4} are hydrogen (see T.H. Mourey *et al.*, J. Appl. Polym. Sci., 45, 1983 (1992), and M. Takayanagi *et al.*, J. Polym. Sci., Polym. Chem.

Ed., 19, 1133 (1981)).

And it is also possible to prepare that desired substituting radical can be introduced at N of diamine monomer compound described below and the desired compound can be prepared by the polymerization reaction by using obtained compound as a monomer.

Example of monomer compound for the production of di-carboxylic acid component corresponding to R^{10} in the general formula (18) above are aromatic group or aromatic containing di-carboxylic acid and their acid halide and alkylesterification product such as terephthalic acid, isophthalic acid, 2-methyl-isophthalic acid, 4-methyl-isophthalic acid, 5-methyl-isophthalic acid, 5-aryloxyisophthalic acid, 5-aryloxycarbonylisophthalic acid, 5-propoxyisophthalic acid, 5-acetyloxyisophthalic acid, 5-benzoylaminoisophthalic acid, tetrafluoroisophthalic acid, methylterephthalic acid, tetraorthoterephthalic acid, tetrafluoroisophthalic acid, methylterephthalic acid, tetrafluoroterephthalic acid, 2,6-naphthalene dicarboxylic acid, 1,6-naphthalene dicarboxylic acid, 2,6-anthracene dicarboxylic acid, 1,6-anthracene dicarboxylic acid, 4,4'-dicarboxy biphenyl, 3,4'-dicarboxy biphenyl, 2,3'-dicarboxy biphenyl, 2,4'-dicarboxy biphenyl, 4,4'-dicarboxy diphenylether, 3,4'-dicarboxy diphenylether, 2,3'-dicarboxy diphenylether, 2,4'-dicarboxy diphenylether, 3,3'-dicarboxy diphenylether, 3,3'-dimethyl-4,4'-dicarboxy biphenyl, 4,4'-dimethyl-3,3'-dicarboxy biphenyl, 2,2'-dimethyl-4,4'-dicarboxy biphenyl, 3,3'-dimethoxy-4,4'-dicarboxy biphenyl, 4,4'-dimethoxy-3,3'-dicarboxy biphenyl, 2,2'-dimethoxy-4,4'-dicarboxy biphenyl, 4,4'-dicarboxy benzophenone, 3,4'-dicarboxy benzophenone, 3,3'-dicarboxy benzophenone, 4,4'-dicarboxy diphenylmethane, 3,4'-dicarboxy diphenylmethane, 3,3'-dicarboxy diphenylmethane, 3,3'-dimethyl-4,4'-dicarboxy diphenylmethane, 2,2'-dimethyl-4,4'-dicarboxy diphenylmethane, 4,4'-dimethyl-3,3'-dicarboxy diphenylmethane, 3,3'-dimethoxy-4,4'-dicarboxy diphenylmethane, 2,2'-dimethoxy-4,4'-dicarboxy diphenylmethane, 4,4'-dimethoxy-3,3'-dicarboxy diphenylmethane, 4,4'-dicarboxy benzanilide, 3,4'-dicarboxy benzanilide, 4,4'-dicarboxy diphenylsulfon, 3,4'-dicarboxy diphenylsulfon, 3,3'-dicarboxy diphenylsulfone, 2,2-bis (4-carboxyphenyl) propane, 1,4-bis (4-carboxyphenoxy) benzene, 1,3-bis (4-carboxyphenoxy) benzene, 1,3-bis (4-carboxybenzamide) benzene, 1,4-bis (4-carboxybenzamide) benzene, bis (4-carboxyphenoxyphenyl) methane, 4,4'-bis

diaminobiphenyl, 4,4'-diaminobenzophenone, 3,4'-diaminobenzophenone, 3,3'-diaminobenzophenone, 4,4'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane, 3,3'-diaminodiphenylmethane, 3,3'-dimethyl-4,4'-diaminodiphenylmethane, 4,4'-dimethyl-3,3'-diaminodiphenylmethane, 2,2'-dimethyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetramethyl-4,4'-diaminodiphenylmethane, 3,3'-dimethoxy-4,4'-diaminodiphenylmethane, 4,4'-dimethoxy-3,3'-diaminodiphenylmethane, 2,2'-dimethoxy-4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylethane, 4,4'-diaminodiphenylamine, 3,4'-diaminodiphenylamine, 4,4'-diaminobenzanilide, 3,4'-diaminobenzanilide, 4,4'-diaminodiphenylsulfone, 3,4'-diaminodiphenylsulfone, 3,3'-diaminodiphenylsulfone, 2,2'-diaminodiphenylpropane, 1,4-bis (4-aminophenoxy) benzene, 1,3-bis (4-aminophenoxy) benzene, 1,3-bis (4-aminobenzamide) benzene, 1,4-bis (4-aminobenzamide) benzene, 4,4'-(4-aminophenoxyphenyl) methane, 4,4'-bis (4-aminophenoxy) diphenylsulfone, 2,2-bis [4-(4-aminophenoxy) phenyl] propane, 2,2-bis (4-aminophenyl) hexafluoropropane, 2,2-bis [4-(4-aminophenoxy) phenyl] hexafluoropropane, 1,5-bis (4-aminophenyl) pentane, 1,4-bis (4-aminophenyl) butane, 1,3-bis (4-aminophenyl) propane, di (4-aminophenyl) pentane-1,5-dioate, di (4-aminophenyl) hexane-1,6-dioate or di (4-aminophenyl) heptane-1,7-dioate. At the same time, diamine having long chain alkyl radical such as 4,4'-diamino-3-dodecylphenylether or 1-dodecyloxy-2,4-diaminobenzene can be used in order to elevate pre-tilt angle. The mixture of more than two kinds can also be used.

The use of diamine compound such as p-phenylenediamine, m-phenylenediamine, methyl-p-phenylenediamine, 4-methyl-m-phenylenediamine, 2,4,6-trimethyl-m-phenylenediamine, 4,4'-diaminobiphenyl, 3,3'-dimethyl-4,4'-diaminobiphenyl, 4,4'-diaminodiphenylether, 4,4'-diaminodiphenylmethane, 3,3'-dimethyl-4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulfone, 2,2-bis [4-(4-aminophenoxy) phenyl] propane is preferred from the standpoint of sensitivity to photo reaction as well as easy availability of raw materials.

Example of monomer compound for the production of aminocarboxylic acid component corresponding to R¹² and R¹³ in the general formula (19a) and (19b) above are aromatic group or aromatic group containing aminocarboxylic acid compound such as m-aminobenzoic acid, p-aminobenzoic acid, 4-methyl-m-

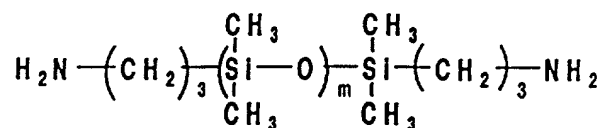
aminobenzoic acid, 3-methyl-p-aminobenzoic acid, 2-amino-6-carboxynaphthalene, 1-amino-5-carboxynaphthalene, 1-amino-6-carboxyanthracene, 2-amino-7-carboxyanthracene, 4-(4-aminophenyl) benzoic acid, 3-(4-aminophenyl) benzoic acid, 4-(3-aminophenyl) benzoic acid, 4-(4-aminophenoxy) benzoic acid, 3-(4-aminophenoxy) benzoic acid, 4-(3-aminophenoxy) benzoic acid, 4-amino-4'-carboxybenzophenone, 3-amino-4'-carboxybenzophenone, 4-amino-3'-carboxybenzophenone, 4-(4-amino-3-methylphenyl) o-toluic acid, 4-(4-amino-2-methylphenyl) o-toluic acid, 4-aminophenyl-4-carboxyphenylmethane, 3-aminophenyl-4-carboxyphenylmethane, 4-aminophenyl-3-carboxyphenylmethane, 4-amino-4'-carboxydiphenylmethane, 4-aminophenyl-4-carboxyphenylsulfone, 3-aminophenyl-4-carboxyphenylsulfone, 4-aminophenyl-3-carboxyphenylsulfone, 2,2-(4-aminophenyl-4-carboxyphenyl) propane, 2,2-(3-aminophenyl-4-carboxyphenyl) propane, 2,2-(4-aminophenyl-3-carboxyphenyl) propane, 4-aminophenyl-4-carboxybenzanilide, 3-amino-4'-carboxybenzanilide, 4-amino-3'-carboxybenzanilide, 4-[3-(4-aminophenoxy) phenoxy] benzoic acid, 4-[4-(4-aminophenoxy) phenoxy] benzoic acid, 1-(4-aminobenzamide)-3-(4-carboxybenzamide) benzene, 1-(4-aminobenzamide)-4-(4-carboxybenzamide) benzene, 4-[4-(4-aminophenoxy) phenyl] benzoic acid, 4-[4-{4-(4-aminophenoxy) phenyl} phenoxy] benzoic acid, 4-[4-[2-{4-(4-aminophenoxy) phenyl} isopropylidene] phenoxy] benzoic acid, 4-[4-[2-{4-(4-aminophenoxy) phenyl} hexafluoroisopropylidene] phenoxy] benzoic acid, 4-[4-(4-aminophenoxy) butoxy] benzoic acid, 4-[5-(4-aminophenoxy) pentyloxy] benzoic acid, 4-[6-(4-aminophenoxy) hexyloxy] benzoic acid, 4-[5-(4-aminophenoxy)-1,5-dioxopentyl] benzoic acid, 4-[6-(4-aminophenoxy)-1,6-dioxohexyl] benzoic acid or 4-[7-(4-aminophenoxy)-1,7-dioxoheptyl] benzoic acid, and in addition alicyclic aminocarboxylic acid such as 3-aminocyclohexane carboxylic acid, 4-aminocyclohexane carboxylic acid, 1-aminocyclobutane carboxylic acid, 2-aminocyclobutane carboxylic acid, 4-(4-aminocyclohexylmethyl) cyclohexane carboxylic acid, 4-(4-amino-3-methylcyclohexylmethyl)-3-methyl-cyclohexane carboxylic acid, 4-(4-aminocyclohexyloxy) cyclohexane carboxylic acid or 4-(4-amino-3-methylcyclohexyloxy)-3-methyl-cyclohexane carboxylic acid. In addition, the mixture of more than two of these compounds can be used.

The use of amino carboxylic acid compound such as p-amino benzoic acid, m-amino benzoic acid, methyl-p-amino benzoic acid, 4-methyl-m-amino benzoic

acid, 4-(4-aminophenoxy) benzoic acid, 3,3'-dimethyl-4-(4'-aminophenyl) benzoic acid, 4-(4-aminophenyl) benzoic acid, (4-aminophenyl-4'-carboxyphenyl) methane, 3,3'-dimethyl-(4-aminophenyl-4'-carboxyphenyl) methane or 4-aminophenyl-4-carboxyphenylsulfone is preferred from the standpoint of sensitivity to photo reaction as well as easy availability of raw materials.

The amount of the repeating unit structure consisting of the structure with divalent or trivalent aromatic group forming the direct bond at amide group, or either divalent or trivalent aromatic group making the direct bond at one end while at the other forming the direct bond with divalent or trivalent alicyclic hydrocarbon is preferably 20 - 100 mole %, more preferably 50 - 100 mole % from the consideration in achieving stable liquid crystal-alignment.

Polyamide as a polymer compound of the present invention can have the structure with the direct bond with divalent or trivalent aromatic group at the both ends of amide group, or either divalent or trivalent aromatic group making the direct bond at one end while at the other forming the direct bond with divalent or trivalent alicyclic hydrocarbon, and dicarboxylic acid, diamine and aminocarboxylic acid without aromatic or alicyclic hydrocarbon groups can also be used together in combination with compounds listed above. Positively identified example are oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, 1,9-nonanedicarboxylic acid or 1,10-decanedicarboxylic acid and their acid halide, acid anhydride or alkylesterification compound as dicarboxylic acid component. The mixture of more than two compounds can also be used. In addition, the component of diamine compound can be aliphatic diamine such as 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 1,7-diaminoheptane, 1,8-diaminooctane, 1,9-diaminononane or 1,10-diaminodecane, and further diaminosiloxane such as m-xylylenediamine, p-xylylenediamine or



wherein m is an integer of 1-10. One or the mixture of more than two compounds selected from these diamine compound can be used.

Aliphatic aminocarboxylic acid components are for example 3-aminopropionic acid, 4-aminobutyric acid, 5-aminopentanoic acid, 6-aminohexanoic acid, 7-aminoheptanoic acid, 8-aminooctanoic acid, 9-aminononanoic acid, 10-aminodecanoic acid or 11-aminoundecanoic acid as aminocarboxylic acid component, and the mixture of more than two compounds selected from these aminocarboxylic acids can be used.

The way to synthesize these polyamide have no limitation. In general, the final product can be obtained either by polycondensation reaction in organic solvent upon charging equimolar ratio of dicarboxylic acid or their derivatives and diamine, by polycondensation reaction with one kind of aminocarboxylic acid or by copolymerization reaction with more than two kinds of aminocarboxylic acids.

These polycondensation reaction proceeds well under the existence of condensation agent, and examples of condensation agent used herewith are triphenyl phosphite, tetrachlorosilane or dimethylchlorosilane among others when dicarboxylic acid or aminocarboxylic acid are used as monomers or trimethylamine, pyridine or N,N-dimethylaniline among others when dicarboxylic acid halide are used as monomer.

Reaction should preferably be carried out in organic solvent, and solvent normally used in the embodiments is for example N,N-dimethyl formamide, N,N-dimethyl acetoamide, N-methyl-2-pyrrolidone, N-methyl caprolactam, tetrahydrofuran, dioxane, toluene, chloroform, dimethylsulfoxide, tetramethyl urea, pyridine, dimethylsulfone, hexamethylphosphoramide, and butyllactone or cresol.

The preferable range of temperature in carrying out condensation reaction is about -100°C to 200°C .

On the other hand, when said dicarboxylic acid anhydride or alkylester compounds are used as monomer, polycondensation reaction in general

proceeds well by mixing diamine compounds and then melting in vacuo without the use of said condensation agent and solvent.

It is important that number-average molecular weight of polyamide obtained by the method of preparation described above is between 1,000 – 300,000, more preferably between 3,000 – 300,000, in order to make the full use of polymer characteristics. Molecular weight was determined by the known methods such as gel permeation chromatography, osmometry, light dispersion, and viscometric molecular weight determination.

When the polyamide film is to be formed, said polyamide film can be formed by applying polymerization solution directly over the substrate and heated. In addition, they can be used after pouring the formed polyamide solution into over excess amount of poor solvents such as water or methanol, and re-dissolve into the solvent after precipitation recovery. The diluting solution of said polyamide solution and/or solvent in which polyamide is re-dissolved after precipitation recovery have no limitation as long as they can dissolve polyamide.

Example of such solvents are 2-pyrrolidone, N-methyl pyrrolidone, N-ethyl pyrrolidone, N-vinyl pyrrolidone, N,N-dimethyl acetoamide, N,N-dimethyl formamide or γ -butyllactone. They can be used by itself or a mixture thereof. In addition, even when said solvent alone can not give homogenous solution, the solvent can be added and used within the range in which homogeneous solution can be obtained. Example of such are ethyl cellosolve, butyl cellosolve, ethyl carbitol, butyl carbitol, ethyl carbitolacetate or ethyleneglycol.

The liquid solution is applied on the substrate, thereby forming the polyamide film over the substrate by the evaporation of solvent. Temperature for this purpose is adequate if solvent can evaporate, and preferred temperature is normally 80 - 200°C.

The liquid solution of the liquid crystal-aligning agent thus obtained in the present invention is applied on the substrate by the method such as spincoat or offset printing, thereby forming the thin polymer film by heating under the condition described above. The thickness of the thin polymer film formed have

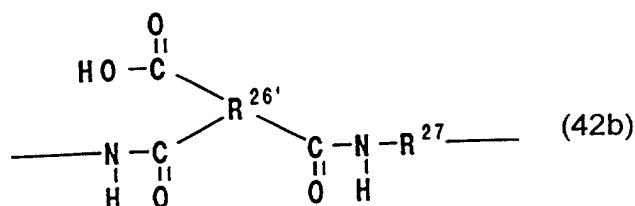
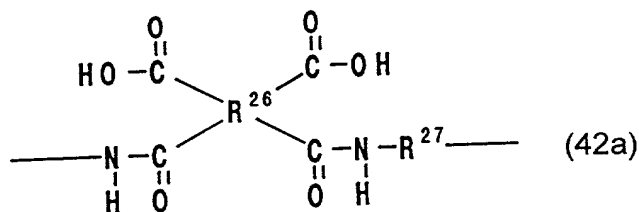
polymer film formed have no special limitation, but 10-3,000nm is preferred for the use in the ordinary liquid crystal-alignment film.

Next, light or electron rays is irradiated over the surface of said thin polymer film. There is no limitation for the wavelength of light used, but in general the range preferred is between 100 nm and 400 nm , more preferably appropriate wavelength should be selected as such with filter and the like depending on the kind of polymer used. In addition, the duration of light irradiation is in general ranging from a couple of minutes to a couple of hours, but it is possible to select suitable time for the polymer to be used.

Further, the way to irradiate have no limitation, but it is preferred to use polarized light in order to obtain the uniform liquid crystal-alignment. In this case, the way to irradiate polarized ultraviolet light have no special limitation. Irradiation can be done with polarized phase being rotated or irradiation can also be done more than twice after changing angles of incidence of polarized ultraviolet rays. Even non-polarized ultraviolet rays may be irradiated at the certain inclination angle from the normal of the substrate as long as practical polarization can be achieved.

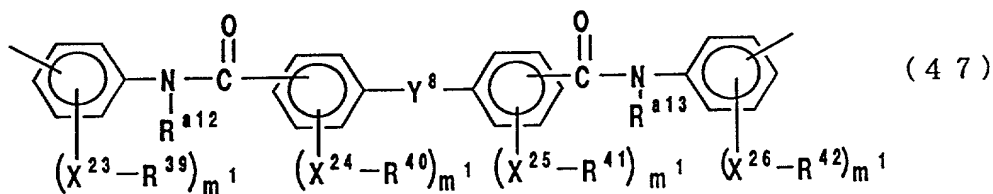
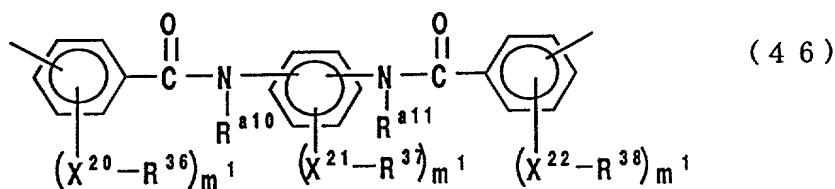
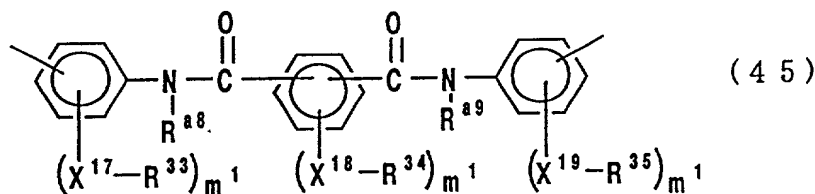
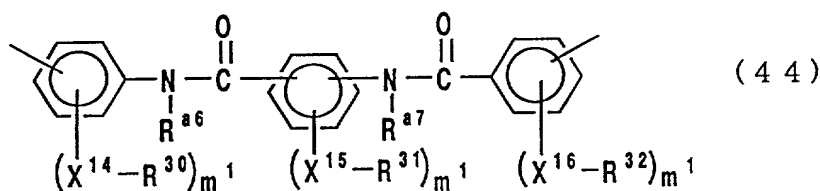
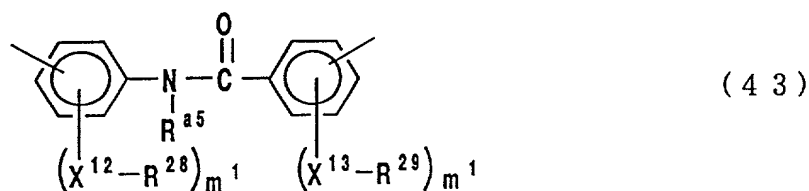
Filmed sides of two substrates thus obtained after irradiation with polarized light are positioned to facing each other and thereby aligning liquid crystal molecules by holding the liquid crystals tightly, and the alignment of the liquid crystals thus obtained is heat stable.

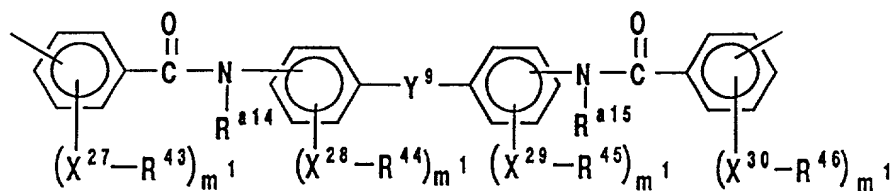
Good examples of polymer compounds of the present invention include polyimide precursor in the general formula (42a) and (42b) below



wherein R^{26} is tetravalent organic radical, $R^{26'}$ is trivalent organic radical, and R^{27} is divalent or trivalent aromatic group or divalent organic radical having amide group bonded with alicyclic hydrocarbon, and polyimide obtained by chemical or heat imidization of said polyimide precursor.

Radical R^{27} of compound in the general formula (42a) and (42b) is preferably selected from radical below in the general formula (43) – (48)





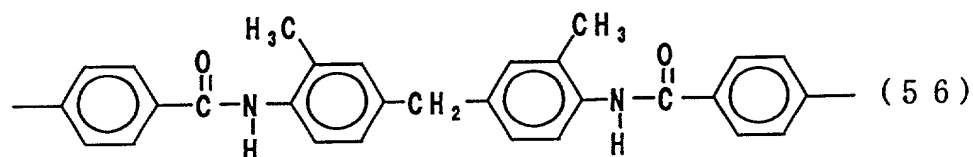
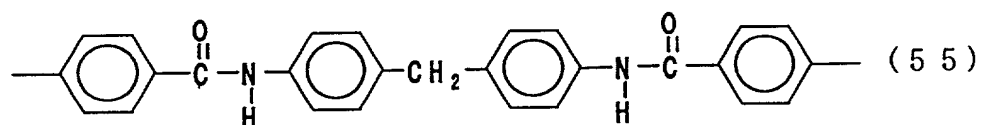
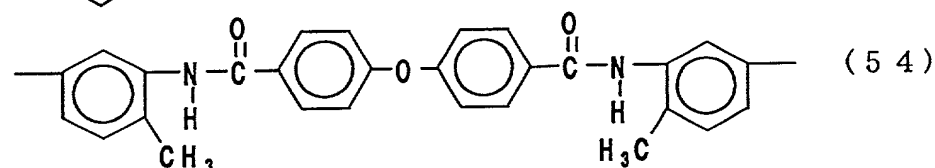
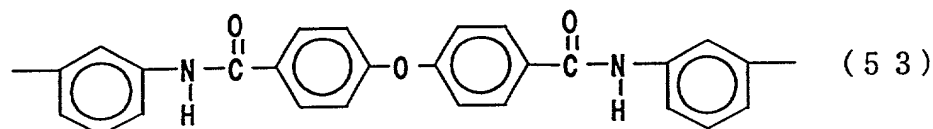
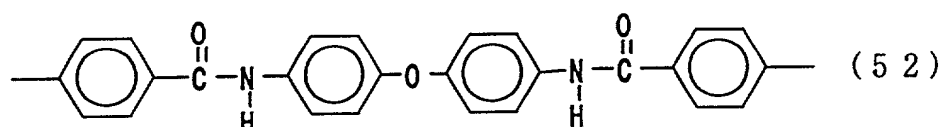
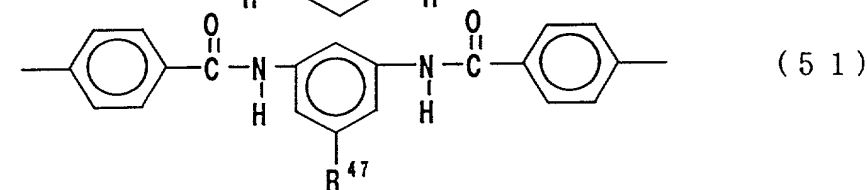
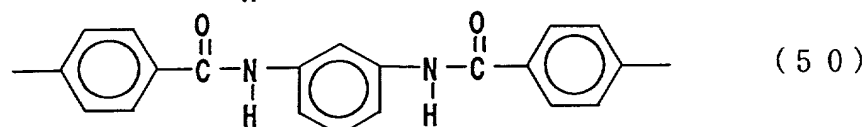
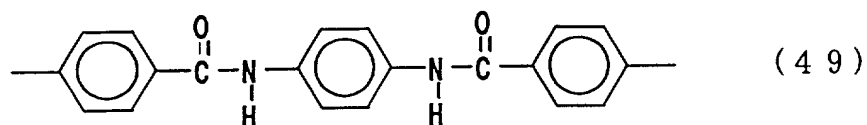
(48)

wherein $X^{12} - X^{30}$ are independently of each other single bond, O, CO_2 , OCO or CH_2O ; $R^{28} - R^{46}$ are independently of each other hydrogen, halogen, $\text{C}_1\text{-C}_{24}$ alkyl, $\text{C}_1\text{-C}_{24}$ alkyl containing fluorine, aryl, propargyl, phenyl or substituted phenyl; $R^{a5} - R^{a15}$ are independently of each other hydrogen, alkyl, substituted alkyl, aryl or propargyl; Y^8 and Y^9 are O, S, SO_2 , CH_2 , NH, NHCO or CONH; and m^1 is an integer of 1 - 4 with the proviso that when $R^{28} - R^{46}$ are hydrogen or halogen, $X^{12} - X^{30}$ are single bond.

Alkyl radical of $\text{C}_1\text{-C}_{24}$ on $R^{28} - R^{46}$ in the general formula above are in addition to lower alkyl such as methyl, ethyl, propyl, i-propyl, butyl, i-butyl, s-butyl and t-butyl, and alkyl group including alicyclic hydrocarbon such as normally used long chain alkyl and cyclohexyl or bicyclohexyl radical. Example of fluorine containing alkyl radical are in addition to lower fluorine containing alkyl such as trifluoromethyl, 2,2,2-trifluoroethyl, perfluoroethyl, 3,3,3-trifluoropropyl, perfluoropropyl, hexafluoro-i-propyl, 3,3,4,4,4-pentafluorobutyl and perfluorobutyl, and normally used long chain fluorine containing alkyl radical. Example of substituting radical for substituted phenyl is halogen, alkyl, fluorine containing alkyl, alkoxy, fluorine containing alkoxy, alkoxycarbonyl or fluorine containing alkoxycarbonyl.

Radical of $R^{a5} - R^{a15}$ in the general formula above are the same as radical of R^1 in the general formula (1) above. Polyimide precursor above and polyimide having radical other than hydrogen at radical of $R^{a5} - R^{a15}$ can be produced by introducing desired substituting radical in advance at N position of amide radical of diamine monomer compound exemplified below, and by carrying out polymerization reaction using thus obtained compound above as a monomer.

In addition, preferred example of radical R^{27} is radical in general formula (49) - (56)

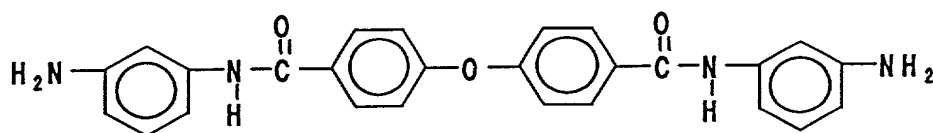
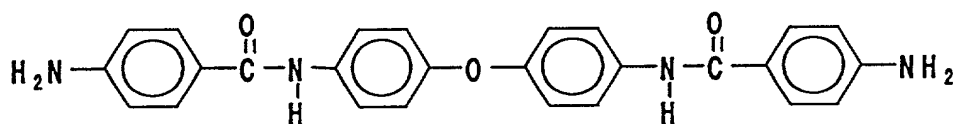
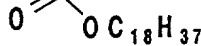
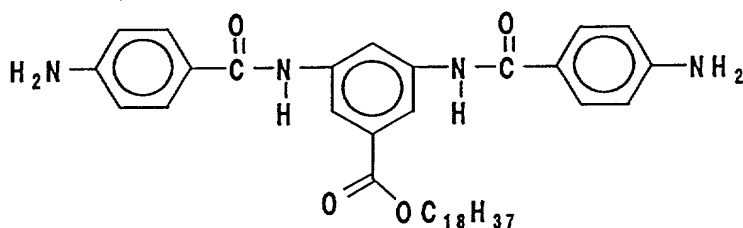
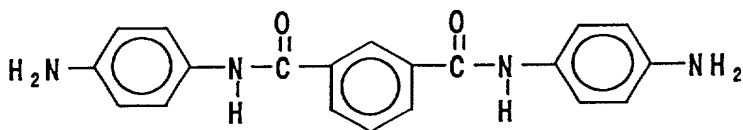
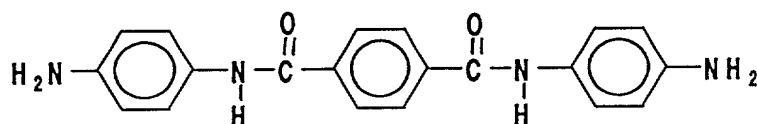


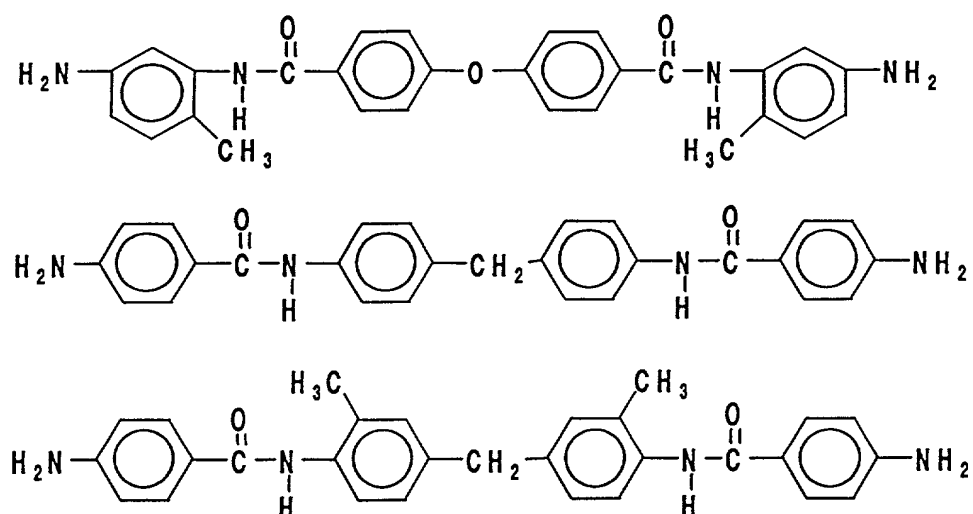
wherein R⁴⁷ in the formula (51) is halogen, C₁-C₂₄ alkyl, C₁-C₂₄ alkoxy or C₁-C₂₄ alkoxycarbonyl.

C₁-C₂₄ alkyl radical of R⁴⁷ in the general formula (51) above are in addition to lower alkyl such as methyl, ethyl, propyl, i-propyl, butyl, i-butyl, s-butyl and t-butyl, and alkyl group including alicyclic hydrocarbon such as normally used long chain alkyl, and cyclohexyl or bicyclohexyl. Example of C₁-C₂₄ alkoxy radical

tricarboxylic acid, 2,3,6-anthracene tricarboxylic acid, 1,2,5-anthracene tricarboxylic acid, 4-(3,4-dicarboxyphenyl) benzoic acid, 3-(3,4-dicarboxyphenyl) benzoic acid, 4-(3,4-dicarboxyphenoxy) benzoic acid, 3-(3,4-dicarboxyphenoxy) benzoic acid, 3,4,4'-benzophenone tricarboxylic acid, 4-carboxyphenyl-3',4'-dicarboxyphenylsulfone, 4-carboxyphenyl-3',4'-dicarboxyphenylmethane and their anhydride and dicarboxylic acid acid halide, and aliphatic tricarboxylic acid such as 1,2,4-butane tricarboxylic acid and their anhydride and these dicarboxylic acid acid halide. In addition, one or more than two compounds selected from these tricarboxylic acid and their derivatives can be used in the mixture.

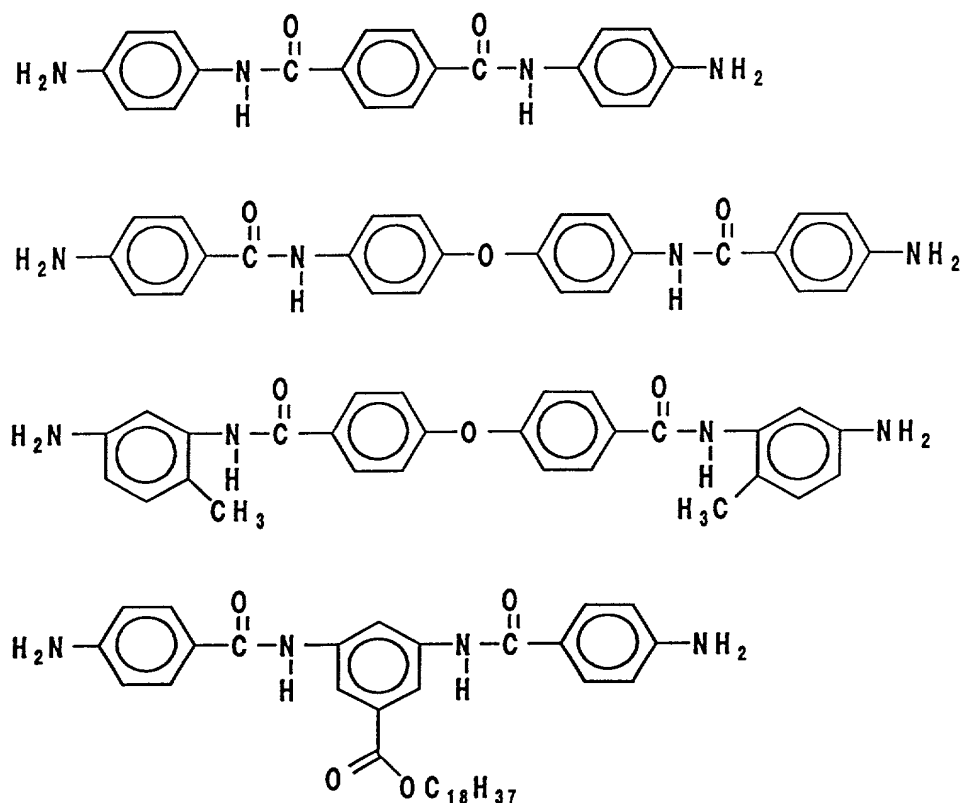
Typical example of monomer compound in making diamine component of R^{27} in general formula (42a) and (42b) above are 4,4'-diaminobenzanilide, 3,4'-diaminobenzanilide, 1,3-di [4-aminobenzamide] benzene, 1,4-di [4-aminobenzamide] benzene and diamine in general formula as illustrated below.





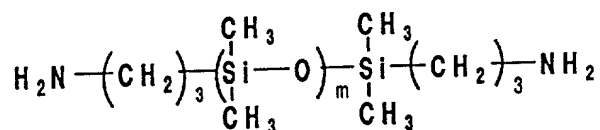
More than two kinds of diamine component can be also mixed for the use.

Additionally, it is preferred to include 4,4'-diaminobenzanilide, 1,3-di [4-aminobenzamide] benzene and diamine components as shown in the general formula below from the viewpoint of stability for liquid crystal-alignment.



forming the direct bond at the both ends of amide radical described above, or either divalent or trivalent aromatic group making the direct bond at one end while at the other forming the direct bond with divalent or trivalent alicyclic hydrocarbon are preferably included as much as 20 to 100 mole %, more preferably 50 to 100 mole % of the total polymer component in view of the stabilization of liquid crystal-alignment.

Further, diamine component generally used in polyimide synthesis can be used as long as they are within the range of manifesting the effect of the present invention. Typical example as such are aromatic diamine such as p-phenylene diamine, m-phenylene diamine, 2,5-diaminotoluene, 2,6-diaminotoluene, 4,4'-diaminobiphenyl, 3,3'-dimethyl-4,4'-diaminobiphenyl, 3,3'-dimethoxy-4,4'-diaminobiphenyl, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylether, 2,2-bis (4-aminophenyl) propane, bis (4-amino-3,5-diethylphenyl) methane, 4,4'-diaminodiphenylsulfone, 4,4'-diaminobenzophenone, 2,6-diaminonaphthalene, 1,4-bis (4-aminophenoxy) benzene, 1,4-bis (4-aminophenyl) benzene, 9,10-bis (4-aminophenyl) anthracene, 1,3-bis (4-aminophenoxy) benzene, 4,4'-di (4-aminophenyl) diphenylsulfone, 2,2-bis [4-(4-aminophenoxy) phenyl] propane, 2,2-bis (4-aminophenyl) hexafluoropropane and 2,2-bis [4-(4-aminophenoxy) phenyl] hexafluoropropane, alicyclic diamine such as bis (4-aminocyclohexyl) methane and bis (4-amino-3-methylcyclohexyl) methane, and aliphatic diamine such as 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 1,7-diaminoheptane, 1,8-diaminooctane, 1,9-diaminononane and 1,10-diaminodecane, and in addition, diamino siloxane such as m-xylelenediamine, p-xylelenediamine or general formula



wherein m is an integer of 1-10.

Moreover, diamine having long chain alkyl group such as 4,4'-diamino-3-dodecyldiphenylether and 1-dodecyloxy-2,4-diaminobenzene can be used in order to elevate the pre-tilt angle. One or more than two kinds of these diamine components can be used in the mixture.

The method of preparation of these polyimide have no special limitation. In general, tetracarboxylic acid and their derivatives are reacted with diamine and polymerized to yield polyimide precursor and then imidization is done by ring closure, and tetracarboxylic acid dianhydride is in general used as tetracarboxylic acid and their derivatives for this purpose. The ratio of tetracarboxylic acid dianhydride mole number and the total mole number of diamine is preferably 0.8 to 1.2. The more this molar ratio approaches closer to 1, the more the polymerization degree of polymer becomes as in general polycondensation reaction.

When polymerization degree is too small, the strength of the polyimide film is unsatisfactory for the use and liquid crystal alignment becomes unstable. But if polymerization degree becomes too large, workability during the polyimide film formation may be poor. Therefore, it is important that number-average molecular weight of polyimide according to the present invention is preferably 1,000 to 300,000, more preferably 3,000 to 300,000, in order to manifest special characteristics of polymer. Molecular weight can be determined by the known methods such as gel permeation chromatography, osmometry, light dispersion method, and viscometric molecular weight determination.

The method of reaction/polymerization of tetracarboxylic acid dianhydride and diamine have no specific limitation, and in general first class diamine and tetracarboxylic acid dianhydride are reacted in organic polar solvent such as N-methyl-2-pyrrolidone, N,N-dimethylacetoamide or N,N-dimethylformamide to yield polyimide precursor and then imidization through dehydration ring closure.

Reaction polymerization temperature of tetracarboxylic acid and their derivatives and diamine can be optional temperature selected from $-20 - 150^{\circ}\text{C}$, but most preferably $-5 - 100^{\circ}\text{C}$. In addition, this polyimide precursor can be imidized by heat dehydration at $100 - 400^{\circ}\text{C}$ or by chemical imidization by the use of imidization catalyst such as triethylamine/acetic anhydride as done under normal condition.

When the polyimide film is to be formed, said polyimide film can be formed

by applying polyimide precursor solution directly over the substrate and imidizing by heating. Polymerization solution described above itself can be used as polyimide precursor solution for this occasion or they can be used after pouring the formed polyimide precursor solution into over excess amount of poor solvents such as water or methanol, and re-dissolve into the solvent after precipitation recovery. The diluting solution of said polyimide precursor solution and/or solvent in which polyimide is re-dissolved after precipitation recovery have no limitation as long as they can dissolve polyimide precursor.

Typical example of such solvent is N-methyl-2-pyrrolidone, N,N-dimethylacetamide and N,N-dimethylformamide. They can be used alone or they can be used in a mixture. What is more, even when said solvent alone can not give homogenous solution, the solvent can be added and used within the range in which homogeneous solution can be obtained. Example of such are ethyl cellosolve, butyl cellosolve, ethyl carbitol, butyl carbitol, ethyl carbitolacetate or ethyleneglycol.

Temperature for heat imidization over the substrate is optional temperature selected from 100 - 400°C, and most preferably in the range of 150 - 350°C.

On the other hand, when polyimide is dissolved in solvent, polyimide precursor solution obtained by reacting tetracarboxylic acid dianhydride and diamine can be used as polyimide solution after imidization.

Polyimide solution thus obtained can be used as they are or they can be used after precipitating in poor solvents such as methanol or ethanol, isolating and re-dissolving into the suitable solvent for the use.

Solvent in which obtained polyimide is re-dissolved can be any solvent without any limitation as long as they can dissolve polyimide obtained, but example of such can be 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethylpyrrolidone, N-vinylpyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide and γ -butyrolactone.

Any other solvent which alone can not solubilize polyimide can be added to the solvent described above within the range of which they do not affect solubility.

Variable	Mean	Standard deviation	Minimum	Maximum
Age	34.5	10.2	20	55
Gender	0.5	0.5	0	1
Marital status	0.7	0.5	0	1
Education	12.5	1.5	9	16
Income	1500	500	500	3000
Health status	0.8	0.4	0	1
Employment status	0.6	0.5	0	1
Home ownership	0.9	0.3	0	1
Vehicle ownership	0.7	0.4	0	1
Life satisfaction	4.5	1.0	1	7
Financial satisfaction	3.8	1.2	1	7
Health satisfaction	5.2	0.8	1	7
Relationship satisfaction	4.1	1.1	1	7
Community satisfaction	3.5	1.3	1	7
Overall life satisfaction	4.3	1.0	1	7

[illegible]

Variable	Mean	Standard deviation	Minimum	Maximum
Age	34.5	10.2	20	55
Gender	0.5	0.5	0	1
Marital status	0.7	0.5	0	1
Education	12.5	1.5	9	16
Income	1500	500	500	3000
Health status	0.8	0.4	0	1
Employment status	0.6	0.5	0	1
Home ownership	0.9	0.3	0	1
Vehicle ownership	0.7	0.4	0	1
Life satisfaction	4.5	1.0	1	7
Financial satisfaction	3.8	1.2	1	7
Health satisfaction	5.2	0.8	1	7
Relationship satisfaction	4.1	1.1	1	7
Community satisfaction	3.5	1.3	1	7
Overall life satisfaction	4.3	1.0	1	7

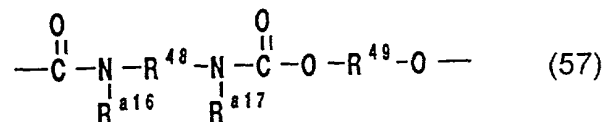
Variable	Mean	SD	Min	Max
Age	34.5	10.2	21	55
Gender	0.45	0.50	0	1
Marital status	0.65	0.48	0	1
Education	12.5	1.5	9	16
Income	1500	500	500	3000
Health status	0.75	0.42	0	1
Employment status	0.85	0.35	0	1
Life satisfaction	4.2	1.8	1	7
Depression	0.35	0.48	0	1
Stress	3.8	1.5	1	6
Quality of life	5.5	2.0	1	9
Physical health	0.85	0.32	0	1
Mental health	0.75	0.40	0	1
Social support	4.5	1.5	1	7
Resilience	3.5	1.2	1	5
Optimism	4.0	1.0	1	5
Gratitude	4.8	1.2	1	6
Forgiveness	4.2	1.5	1	6
Self-esteem	3.8	1.0	1	5
Life purpose	4.5	1.2	1	6
Meaning in life	4.0	1.0	1	5
Existential well-being	4.2	1.2	1	5
Psychological well-being	4.5	1.0	1	5
Overall well-being	4.8	1.2	1	6

Variable	Mean	SD	Min	Max
Age	34.5	10.2	21	55
Gender	0.45	0.50	0	1
Marital status	0.65	0.48	0	1
Education	12.5	1.5	9	16
Income	1500	500	500	3000
Health status	0.75	0.42	0	1
Employment status	0.85	0.35	0	1
Life satisfaction	4.2	1.8	1	7
Depression	0.35	0.48	0	1
Stress	3.8	1.5	1	6
Quality of life	5.5	2.0	1	9
Resilience	4.5	1.5	1	7
Optimism	4.8	1.2	1	7
Self-efficacy	4.0	1.0	1	5
Perceived stress	3.5	1.2	1	5
Life events	2.5	1.0	0	4
Support network	4.0	1.5	1	6
Coping strategies	3.0	1.0	1	4
Healthcare utilization	2.0	1.0	0	3
Health insurance	0.95	0.05	0	1
Access to care	0.80	0.40	0	1
Health literacy	3.5	1.0	1	5
Health beliefs	4.0	1.0	1	5
Health behaviors	3.0	1.0	1	4
Health status (self-reported)	4.5	1.0	1	5
Health status (clinician-reported)	4.0	1.0	1	5
Health status (objective)	4.5	1.0	1	5
Health status (subjective)	4.0	1.0	1	5
Health status (functional)	4.5	1.0	1	5
Health status (quality of life)	4.0	1.0	1	5
Health status (well-being)	4.5	1.0	1	5
Health status (satisfaction)	4.0	1.0	1	5
Health status (engagement)	4.5	1.0	1	5
Health status (participation)	4.0	1.0	1	5
Health status (empowerment)	4.5	1.0	1	5
Health status (self-management)	4.0	1.0	1	5
Health status (decision-making)	4.5	1.0	1	5
Health status (communication)	4.0	1.0	1	5
Health status (relationship)	4.5	1.0	1	5
Health status (trust)	4.0	1.0	1	5
Health status (respect)	4.5	1.0	1	5
Health status (dignity)	4.0	1.0	1	5
Health status (autonomy)	4.5	1.0	1	5
Health status (information)	4.0	1.0	1	5
Health status (education)	4.5	1.0	1	5
Health status (skills)	4.0	1.0	1	5
Health status (knowledge)	4.5	1.0	1	5
Health status (attitudes)	4.0	1.0	1	5
Health status (beliefs)	4.5	1.0	1	5
Health status (values)	4.0	1.0	1	5
Health status (norms)	4.5	1.0	1	5
Health status (culture)	4.0	1.0	1	5
Health status (religion)	4.5	1.0	1	5
Health status (ethnicity)	4.0	1.0	1	5
Health status (language)	4.5	1.0	1	5
Health status (disability)	4.0	1.0	1	5
Health status (chronic illness)	4.5	1.0	1	5
Health status (acute illness)	4.0	1.0	1	5
Health status (injury)	4.5	1.0	1	5
Health status (mental illness)	4.0	1.0	1	5
Health status (substance use)	4.5	1.0	1	5
Health status (lifestyle)	4.0	1.0	1	5
Health status (diet)	4.5	1.0	1	5
Health status (exercise)	4.0	1.0	1	5
Health status (sleep)	4.5	1.0	1	5
Health status (stress management)	4.0	1.0	1	5
Health status (coping)	4.5	1.0	1	5
Health status (resilience)	4.0	1.0	1	5
Health status (optimism)	4.5	1.0	1	5
Health status (self-efficacy)	4.0	1.0	1	5
Health status (perceived stress)	4.5	1.0	1	5
Health status (life events)	4.0	1.0	1	5
Health status (support network)	4.5	1.0	1	5
Health status (coping strategies)	4.0	1.0	1	5
Health status (healthcare utilization)	4.5	1.0	1	5
Health status (health insurance)	4.0	1.0	1	5
Health status (access to care)	4.5	1.0	1	5
Health status (health literacy)	4.0	1.0	1	5
Health status (health beliefs)	4.5	1.0	1	5
Health status (health behaviors)	4.0	1.0	1	5
Health status (health status)	4.5	1.0	1	5
Health status (health status)	4.0	1.0		

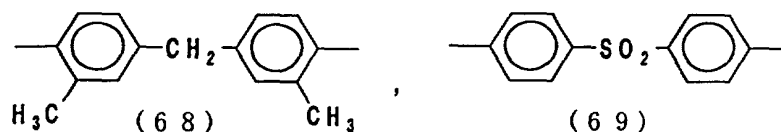
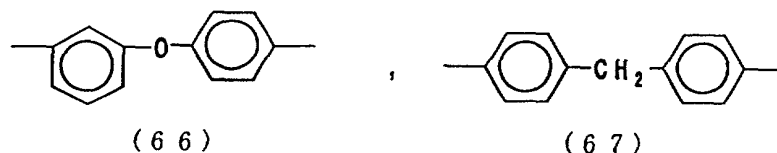
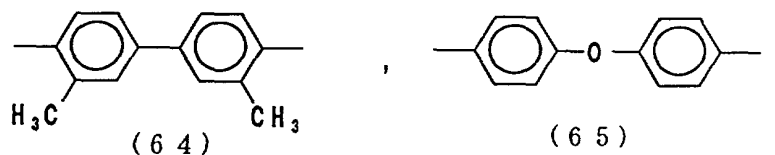
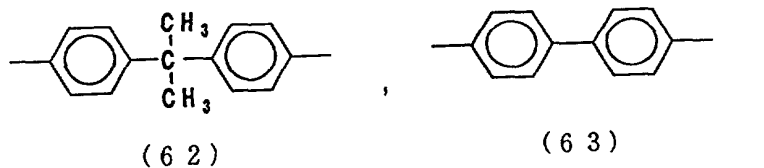
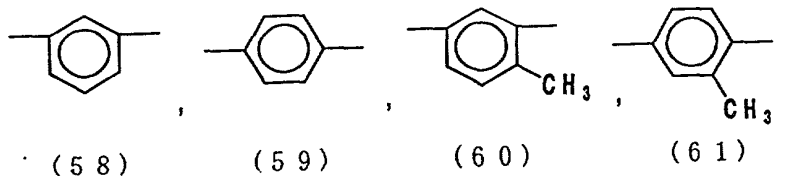
Variable	Mean	Standard deviation	Minimum	Maximum
Age	34.5	10.2	18	65
Gender	0.5	0.5	0	1
Marital status	0.6	0.5	0	1
Education	12.5	1.5	9	16
Income	1500	500	500	3000
Health status	0.8	0.2	0	1
Employment status	0.7	0.5	0	1
Home ownership	0.6	0.5	0	1
Vehicle ownership	0.4	0.5	0	1
Life satisfaction	4.5	1.0	1	7
Subjective health	3.5	1.0	1	5
Life expectancy	75	5	60	90
Quality of life	5.5	1.0	1	7
Healthcare utilization	2.5	1.0	0	4
Health insurance	0.9	0.3	0	1
Healthcare access	0.8	0.2	0	1
Healthcare cost	1000	500	0	2000
Healthcare quality	4.0	1.0	1	5
Healthcare satisfaction	4.5	1.0	1	7
Healthcare equity	4.0	1.0	1	5
Healthcare efficiency	4.0	1.0	1	5
Healthcare effectiveness	4.0	1.0	1	5
Healthcare safety	4.0	1.0	1	5
Healthcare accessibility	4.0	1.0	1	5
Healthcare affordability	4.0	1.0	1	5
Healthcare availability	4.0	1.0	1	5
Healthcare acceptability	4.0	1.0	1	5
Healthcare appropriateness	4.0	1.0	1	5
Healthcare timeliness	4.0	1.0	1	5
Healthcare convenience	4.0	1.0	1	5
Healthcare continuity	4.0	1.0	1	5
Healthcare coordination	4.0	1.0	1	5
Healthcare integration	4.0	1.0	1	5
Healthcare collaboration	4.0	1.0	1	5
Healthcare partnership	4.0	1.0	1	5
Healthcare leadership	4.0	1.0	1	5
Healthcare governance	4.0	1.0	1	5
Healthcare management	4.0	1.0	1	5
Healthcare innovation	4.0	1.0	1	5
Healthcare research	4.0	1.0	1	5
Healthcare education	4.0	1.0	1	5
Healthcare training	4.0	1.0	1	5
Healthcare development	4.0	1.0	1	5
Healthcare reform	4.0	1.0	1	5
Healthcare policy	4.0	1.0	1	5
Healthcare legislation	4.0	1.0	1	5
Healthcare regulation	4.0	1.0	1	5
Healthcare supervision	4.0	1.0	1	5
Healthcare monitoring	4.0	1.0	1	5
Healthcare evaluation	4.0	1.0	1	5
Healthcare assessment	4.0	1.0	1	5
Healthcare audit	4.0	1.0	1	5
Healthcare inspection	4.0	1.0	1	5
Healthcare investigation	4.0	1.0	1	5
Healthcare inquiry	4.0	1.0	1	5
Healthcare consultation	4.0	1.0	1	5
Healthcare advice	4.0	1.0	1	5
Healthcare guidance	4.0	1.0	1	5
Healthcare support	4.0	1.0	1	5
Healthcare assistance	4.0	1.0	1	5
Healthcare help	4.0	1.0	1	5
Healthcare aid	4.0	1.0	1	5
Healthcare relief	4.0	1.0	1	5
Healthcare comfort	4.0	1.0	1	5
Healthcare ease	4.0	1.0	1	5
Healthcare simplicity	4.0	1.0	1	5
Healthcare clarity	4.0	1.0	1	5
Healthcare transparency	4.0	1.0	1	5
Healthcare openness	4.0	1.0	1	5
Healthcare honesty	4.0	1.0	1	5
Healthcare integrity	4.0	1.0	1	5
Healthcare trustworthiness	4.0	1.0	1	5
Healthcare reliability	4.0	1.0	1	5
Healthcare dependability	4.0	1.0	1	5
Healthcare predictability	4.0	1.0	1	5
Healthcare consistency	4.0	1.0	1	5
Healthcare uniformity	4.0	1.0	1	5
Healthcare regularity	4.0	1.0	1	5
Healthcare orderliness	4.0	1.0	1	5
Healthcare neatness	4.0	1.0	1	5
Healthcare tidiness	4.0	1.0	1	5
Healthcare cleanliness	4.0	1.0	1	5
Healthcare hygiene	4.0	1.0	1	5
Healthcare safety	4.0	1.0	1	

molecules by holding the liquid crystals tightly and the alignment of the liquid crystals thus obtained is heat stable.

Preferred example of polymer compound according to the present invention is polyurethane having repeating unit shown in general formula (57) below



wherein R^{48} and R^{49} are independently of each other selected from groups shown in general formula (58) - (69) below



wherein R^{a16} and R^{a17} are independently of each other hydrogen, alkyl, aryl or propagyl.

Radical R^{a16} and R^{a17} in the general formula above are the same as radical R^1 in the general formula (2) above. The polyurethane with radical R^{a16} and R^{a17} which is radical other than hydrogen can be obtained by introducing desired radical at the preferred ratio at N position of urethane radical in polyurethane having radical R^{a16} and R^{a17} which are hydrogen by using the known polymer reaction (T. H. Mourey *et al.*, J. Appl. Polym. Sci., 45, 1983 (1992) and M. Takayanagi *et al.*, J. Polym. Sci., Polym. Chem. Ed., 19, 1133 (1981)).

Typical example of monomer compound in forming diisocyanate corresponding to R^{48} in the general formula (57) above are 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 4-methyl-1,3-phenylene diisocyanate, 5-methyl-1,4-phenylene diisocyanate, 2,2-bis (isocyanatephenyl) propane, 4,4'-diisocyanate biphenyl, 3,3'-dimethyl-4,4'-diisocyanate biphenyl, 4,4'-diisocyanate diphenylether, 3,4'-diisocyanate diphenylether, 4,4'-diisocyanate diphenylmethane, 3,3'-dimethyl-4,4'-diisocyanate diphenylmethane, 4,4'-diisocyanate diphenylsulfone, 1,3-cyclohexane diisocyanate and 1,4-cyclohexane diisocyanate. In addition, the mixture of more than two of these kinds can be used.

On the other hand, typical example of monomer compound in forming diol component corresponding to R^{49} in the general formula (57) above are resorcinol, hydroquinone, 4-methylresorcinol, 5-methylhydroquinone, bisphenol A, 4,4'-biphenol, 3,3'-dimethyl-4,4'-biphenol, 4,4'-dihydroxy diphenylether, 3,4'-dihydroxy diphenylether, 4,4'-dihydroxy diphenylmethane, 3,3'-dimethyl-4,4'-dihydroxy diphenylmethane, 4,4'-dihydroxy diphenylsulfone, 1,3-cyclohexane diol and 1,4-cyclohexane diol as preferred example.

Polyurethane as the polymer compound of the present invention can have the structure with divalent or trivalent aromatic group forming the direct bond at urethane radical, or either divalent or trivalent aromatic group making the direct bond at one end while at the other forming the direct bond with divalent or trivalent alicyclic hydrocarbon, and diisocyanate compound or diol compound without aromatic or alicyclic hydrocarbon can be used together in combination.

Positively identified example as such are tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate and m-xylylene diisocyanate as diisocyanate compound and the mixture of more than two of these kinds can be also used. What is more, example of diol compound are ethyleneglycol, trimethyleneglycol, tetramethyleneglycol, pentamethyleneglycol, hexamethyleneglycol, diethyleneglycol, triethyleneglycol, m-xylyleneglycol and p-xylyleneglycol. One or more than two kinds of these diol components can be mixed for the use.

The way to synthesize these polyurethane have no special limitation. They can be obtained in general by charging equal mole amount of diisocyanate and diol and carrying out polyaddition reaction in organic solvent. These polyaddition reaction can proceed well with catalyst and catalyst preferably used here may be for example triethyamine, tributylamine, diisobutylamine, dibutylamine, diethylamine, pyridine and 2,6-dimethylpyridine.

The reaction is preferably carried out in organic solvent and typical example of solvent used are N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, N-methylcaprolactam, tetrahydrofuran, dioxane, toluene, chloroform, dimethylsulfoxide, tetramethylurea, pyridine, dimethylsulfone, hexamethylphosphoramide, butyllactone and cresol.

The preferable range of polyaddition reaction is the reaction temperature of $-20 - 200^{\circ}\text{C}$.

It is important that number-average molecular weight of polyurethane obtained by the method of the preparation described above is preferably 1,000 to 300,000, more preferably 3,000 to 300,000, in order to manifest special characteristics of polymer. Molecular weight can be determined by the known methods such as gel permeation chromatography, osmometry, light dispersion method, and viscometric molecular weight determination.

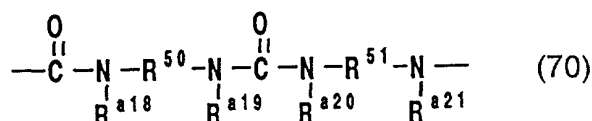
When polyurethane film is to be formed, said polyurethane film can be formed by applying polyurethane solution directly over the substrate and heated. In addition, they can be used after pouring the formed polyurethane solution into over excess amount of poor solvents such as water or methanol, and re-dissolve

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case, the way to irradiate polarized ultraviolet light have no special limitation. Irradiation can be done with polarized phase being rotated, and irradiation can also be done more than twice after changing angles of incidence of polarized ultraviolet rays. Even non-polarized ultraviolet rays may be irradiated at the certain inclination angle from the normal of the substrate as long as practical polarization can be achieved.

Filmed sides of two substrates thus obtained after irradiation with polarized light are positioned at facing each other and thereby aligning liquid crystal molecules by holding the liquid crystals tightly and the alignment of the liquid crystals thus obtained is heat stable.

Good examples of polymer compounds of the present invention are polyurea having the repeating unit shown in the general formula (70) below



wherein R^{50} and R^{51} are independently of each other selected from group in the general formula (58) - (69), and R^{a18} - R^{a21} are hydrogen, alkyl, substituted alkyl, aryl or propargyl.

Radical R^{a18} - R^{a21} in general formula above are the same as radical R^1 and R^2 in the general formula (3) described above. The polyurea with radical R^{a18} - R^{a21} whose radicals are other than hydrogen can be obtained by introducing desired radical at the preferred ratio at N position of urea radical in polyurea having radical R^{a18} - R^{a21} which are hydrogen by using the known polymer reaction (T.H. Mourey *et al.*, J. Appl. Polym. Sci., 45, 1983 (1992) and M. Takayanagi *et al.*, J. Polym. Sci., Polym. Chem. Ed., 19, 1133 (1981)).

Typical example of monomer compound in forming diisocyanate component corresponding to R^{50} in the general formula (70) above are 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 4-methyl-1,3-phenylene diisocyanate, 5-methyl-1,4-phenylene diisocyanate, 2,2-bis (isocyanatephenyl) propane, 4,4'-diisocyanate diphenyl, 3,3'-dimethyl-4,4'-diisocyanate diphenyl,

4,4'-diisocyanate diphenylether, 3,4'-diisocyanate diphenylether, 4,4'-diisocyanate diphenylmethane, 3,3'-dimethyl-4,4'-diisocyanate diphenylmethane, 4,4'-diisocyanate diphenylsulfone, 1,3-cyclohexane diisocyanate and 1,4-cyclohexane diisocyanate. The mixture of more than two of these kinds can be used.

On the other hand, typical example of monomer compound in forming diamine component corresponding to R⁵¹ in general formula (70) above are m-phenylene diamine, p-phenylene diamine, 4-methyl-m-phenylene diamine, 5-methyl-p-phenylene diamine, 2,2-bis (4-aminophenyl) propane, 4,4'-diaminediphenyl, 4,4'-diamino-3,3'-dimethylphenyl, 4,4'-diamino diphenylether, 3,4'-diamino diphenylether, 4,4'-diamino diphenylmethane, 4,4'-diamino-3,3'-dimethyl diphenylmethane, 4,4'-diamino diphenylsulfone and 1,3-cyclohexane diamine. Moreover, the mixture of more than two of these kinds can be used.

Polyurea as a polymer compound of the present invention can have the structure with divalent or trivalent aromatic group forming the direct bond at urea group, or either divalent or trivalent aromatic group making the direct bond at one end while at the other forming the direct bond with divalent or trivalent alicyclic hydrocarbon, and diisocyanate compound and diamine compound can be used together in combination as long as they do not have aromatic or alicyclic hydrocarbon group. Positively identified example as such are tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate and m-xylylene diisocyanate, and the mixture of more than two of these kinds can also be used. Furthermore, aliphatic diamine such as 1,2-diaminoethane, 1,3-diamino propane, 1,4-diamino butane, 1,5-diamino pentane, 1,6-diamino hexane, 1,7-diamino heptane, 1,8-diamino octane, 1,9-diamino nonane and 1,10-diamino decane as diamine compound in addition to m-xylylenediamine and p-xylylenediamine. One or the mixture of more than two of these diamine components can be used.

The way to synthesize these polyurea have no limitation. In general, the final products can be obtained either by the polyaddition reaction in organic solvent upon charging equimolar ratio of diisocyanate and diamine. Solvent normally used in the embodiments are for example N,N-dimethyl formamide, N,N-dimethyl acetoamide, N-methyl-2-pyrrolidone, N-methyl caprolactam,

tetrahydrofuran, dioxane, toluene, chloroform, dimethylsulfoxide, tetramethyl urea, pyridine, dimethylsulfone, hexamethylphosphoramide, butyllactone and cresol.

The preferable range of polyaddition reaction temperature is under the normal circumstances in the range of -20°C and 150°C.

It is important that the number-average molecular weight of polyurea obtained by the method of preparation described above is between 1,000 – 300,000, more preferably between 3,000 – 300,000, in order to make the full use of polymer characteristics. Molecular weight was determined by the known methods such as gel permeation chromatography, osmometry, light dispersion, and viscometric molecular weight determination.

When polyurea film is to be formed, said polymer solution may be directly applied over the substrate and heated to form the polyurethane film. In addition, they can be used after pouring the formed polyurea solution into over excess amount of poor solvents such as water or methanol, and re-dissolve into the solvent after precipitation recovery. The diluting solution of said polyurea solution and/or solvent in which polyurea is re-dissolved after precipitation recovery have no limitation as long as they can dissolve polyurea.

Example of such solvents are 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl pyrrolidone, N-vinyl pyrrolidone, N,N-dimethyl acetoamide, N,N-dimethyl formamide or γ -butyllactone. They can be used by itself or a mixture thereof. In addition, even when said solvent alone can not give homogenous solution, the solvent can be added and used within the range in which homogeneous solution can be obtained. Example of such are ethyl cellosolve, butyl cellosolve, ethyl carbitol, butyl carbitol, ethyl carbitolacetate or ethyleneglycol.

The liquid solution can be applied on the substrate, thereby forming the polyurea film over the substrate by the evaporation of solvent. Temperature for this purpose is adequate if solvent can evaporate, and preferred temperature is normally 80 - 200°C.

The liquid solution of the liquid crystal-alignment agent thus obtained in the

present invention is applied on the substrate by the method such as spincoat or decalcomania process printing, thereby forming the thin polymer film by heat calcination under the condition described above. The thickness of the thin polymer film formed have no special limitation, but 10 - 3,000 nm is preferred for the use in the ordinary liquid crystal alignment film.

Light or electron rays is subsequently irradiated over the surface of said thin polymer film. There is no limitation for the wavelength of light utilized, but in general the range preferred is between 100 nm and 400 nm, more preferably appropriate wavelength should be selected by an appropriate device such as filter depending on the kind of polymer used. In addition, the duration of light irradiation is in general ranging from a couple of minutes to a couple of hours, but it is possible to select suitable length of time for polymer to be used.

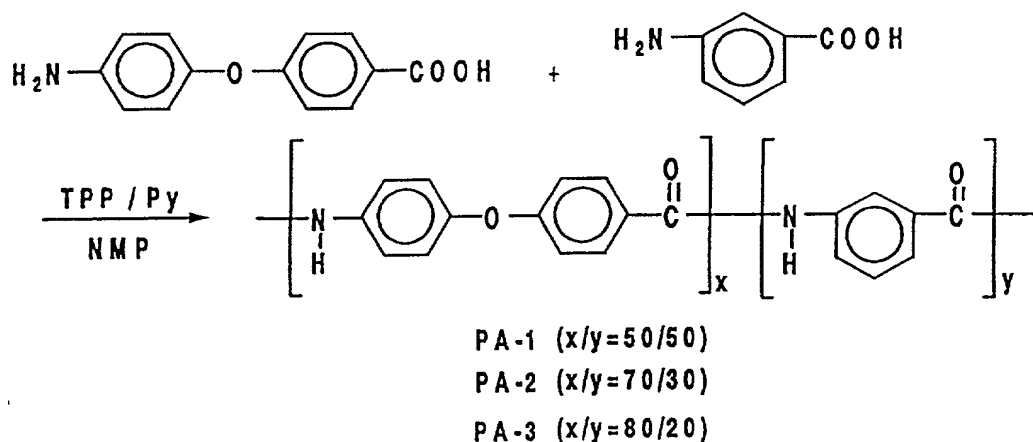
Further, the way to irradiate have no limitation, but it is preferred to use polarized light in order to obtain the uniform liquid crystal-alignment. In this case, the way to irradiate polarized ultraviolet light have no special limitation. Irradiation can be done with polarized phase being rotated, and irradiation can also be done more than twice after changing angles of incidence of polarized ultraviolet rays. Even non-polarized ultraviolet rays may be irradiated at the certain inclination angle from the normal of the substrate as long as practical polarization can be achieved.

Filmed sides of two substrates thus obtained after irradiation with polarized light are positioned to facing each other and thereby aligning liquid crystal molecules by holding the liquid crystals tightly and the alignment of the liquid crystals thus obtained is heat stable.

Best Mode for Carrying Out the Invention

The present invention is described further in more details by showing the examples, references and comparative examples, but the invention is not limited to the particular embodiments described herein.

Example 1-3



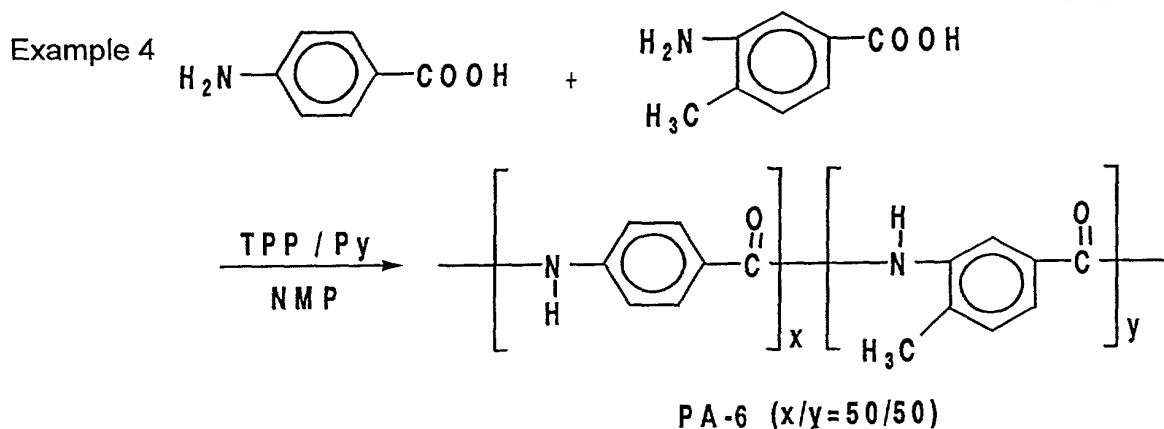
Under nitrogen gas atmosphere, 4-(4-aminophenoxy) benzoic acid (abbreviated as APBA hereafter) and m-amino benzoic acid (abbreviated as MABA hereafter) are mixed together to respective fixed molar ratio, and N-methylpyrrolidone (abbreviated as NMP hereafter) and 1.2 equivalent of pyridine based on total monomer as well as 1.2 equivalent of triphenyl phosphite (abbreviated as Py hereafter) are added, and stirred for the predetermined time after heated to 100°C. Monomer used and described above, amounts of reagent chemicals and solvents, and reaction time are summarized in Table 1 below. Obtained reaction solution is diluted to 7% as to the total solid with the addition of NMP, and then the mixture is poured into excess methanol and polymer precipitated were filtered and dried. The procedures above were repeated, purified, and each polyamide shown in the structural formulas PA-1 to PA-3 above were obtained. Yield of obtained polyamide, number-average molecular weight and weight-average molecular weight obtained through the gel permeation chromatography are shown in Table 2.

Table 1

Example	Amount of APBA g (mmol)	Amount of MABA g (mmol)	Amount of Py ml	Amount of TPP ml	Amount of NMP ml	Reaction time hr
1	27.507 (120)	16.457 (120)	23.29	75.47	146.56	10
2	0.4814 (2.1)	0.1234 (0.9)	0.29	0.94	1.96	8
3	0.5501 (2.4)	0.0823 (0.6)	0.29	0.94	2.12	8

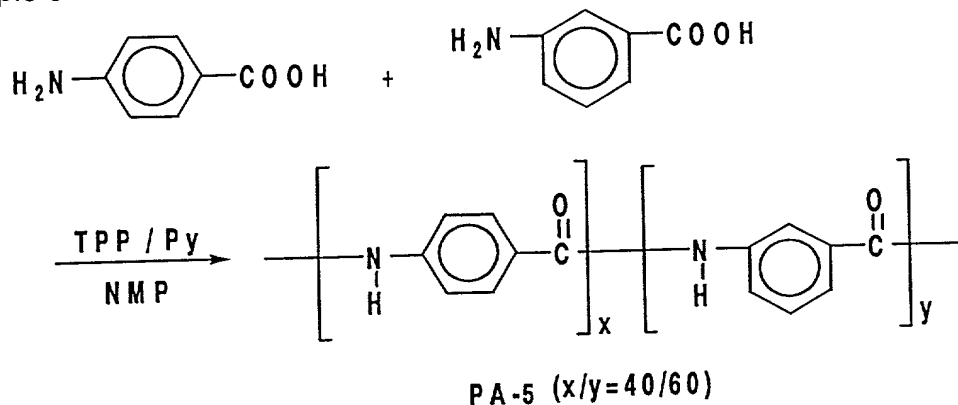
Table 2

Example	Polymer No.	Polymer yield (g)	Number-average molecular weight	Weight-average molecular weight
1	PA-1	33.28	3.08×10^4	5.59×10^4
2	PA-2	0.54	2.11×10^4	3.96×10^4
3	PA-3	0.55	1.85×10^4	3.87×10^4



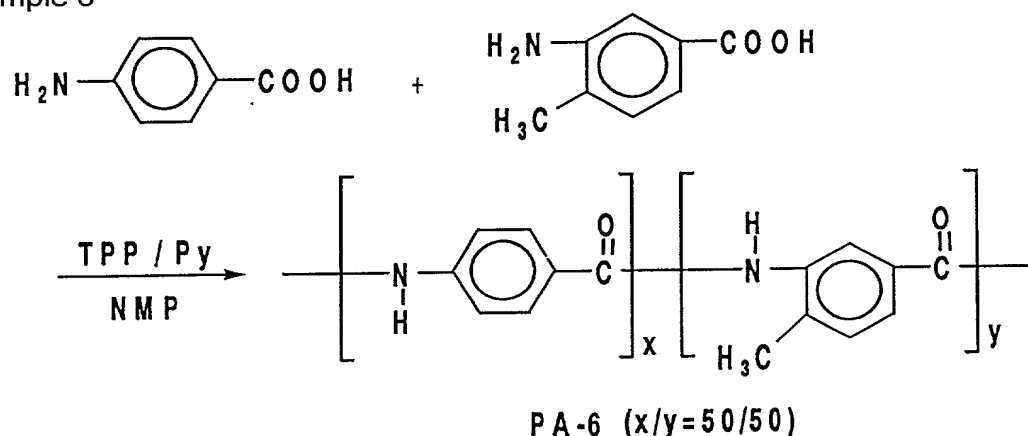
Under nitrogen gas atmosphere, 0.92 g (4 mmol) of APBA and 0.60 g (4 mmol) of 4-methyl-m-aminobenzoic acid (abbreviated as Me-MABA hereafter) were dissolved in 4.75 ml of NMP, and 0.78 ml of Py and 2.52 ml of TPP were added into this liquid solution and stirred for 19 hours after heated to 100°C. Obtained reaction liquid solution was diluted with 11.6 ml of NMP and poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 1.49 g of polyamide shown in the structural formula PA-4 above was obtained. Number-average molecular weight and weight-average molecular weight of PA-4 obtained through the gel permeation chromatography were 1.06×10^4 and 1.89×10^4 , respectively.

Example 5



Under argon gas atmosphere, 0.20 g (1.458 mmol) of p-amino benzoic acid (abbreviated as PABA hereafter) and 0.30 g (2.188 mmol) of MABA were dissolved in 1.31 ml of NMP, and 0.31 ml of Py and 1.00 ml of TPP were added into this liquid solution and stirred for 18 hours after heated to 100°C. The reaction liquid solution thus obtained was diluted with 4 ml of NMP and then poured into 50 ml of excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 0.412 g of polyamide shown in the structural formula PA-5 was obtained. Number-average molecular weight and weight-average molecular weight of PA-5 obtained through the gel permeation chromatography were 6.74×10^3 and 1.26×10^4 , respectively.

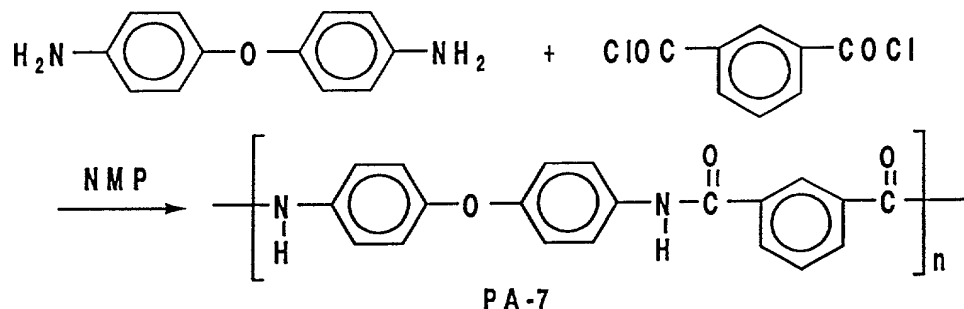
Example 6



Under argon gas atmosphere, 0.27 g (2.0 mmol) of PABA and 0.30 g (2.0 mmol) of Me-MABA were dissolved in 1.33 ml of NMP, and 0.39 ml of Py and 1.26 ml of TPP were added into this liquid solution and stirred for 18 hours after heated to 100°C. Reaction liquid solution thus obtained was diluted with 4 ml of NMP and then poured into 50 ml of excess methanol, and polymer precipitated were filtered

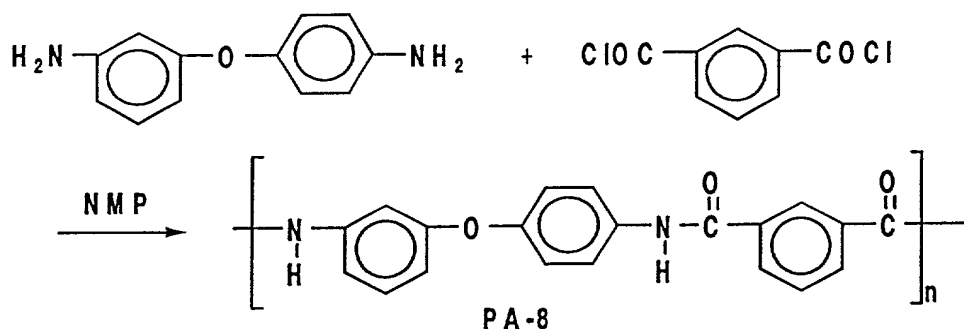
and dried. The procedures above were repeated and purified, and 0.480 g of polyamide shown in the structural formula PA-6 above was obtained. Number-average molecular weight and weight-average molecular weight of PA-6 obtained through the gel permeation chromatography were 7.56×10^3 and 2.52×10^4 , respectively.

Example 7



Under argon gas atmosphere, 2.03 g (10.0 mmol) of isophthalic acid dichloride and 2.00 g (10.0 mmol) of 4,4'-diaminodiphenylether were each dissolved to the concentration of 1.0 mol/l in NMP and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for 30 minutes at room temperature. Reaction liquid solution thus obtained was diluted with 30 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 3.85 g of polyamide shown in the structural formula PA-7 was obtained. Number-average molecular weight and weight-average molecular weight of PA-7 obtained through the gel permeation chromatography were 1.40×10^4 and 2.90×10^4 , respectively.

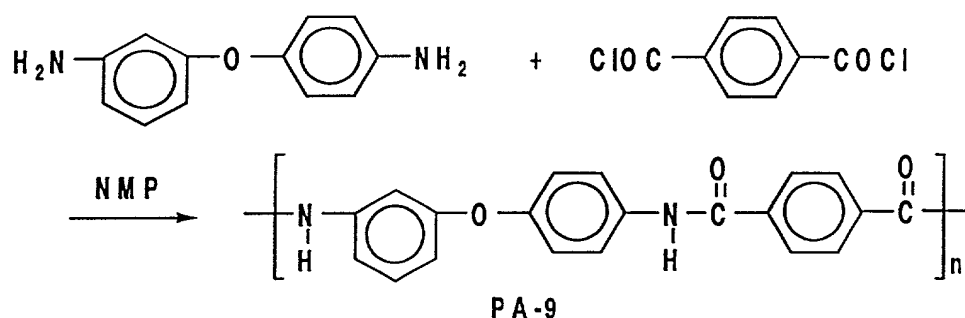
Example 8



Under argon gas atmosphere, 2.03 g (10.0 mmol) of isophthalic acid dichloride and 2.00 g (10.0 mmol) of 3,4'-diaminodiphenylether were each dissolved

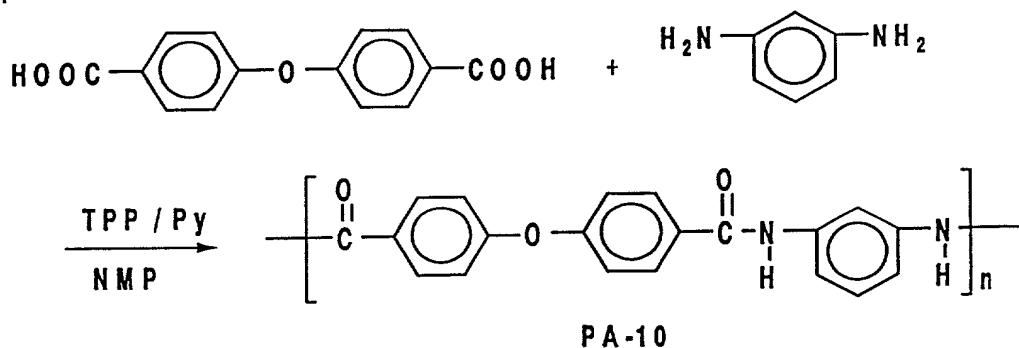
to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for 15 minutes at room temperature. Reaction liquid solution thus obtained was diluted with 30 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 3.82 g of polyamide shown in the structural formula PA-8 was obtained. Number-average molecular weight and weight-average molecular weight of PA-8 obtained through the gel permeation chromatography were 1.32×10^4 and 2.98×10^4 , respectively.

Example 9



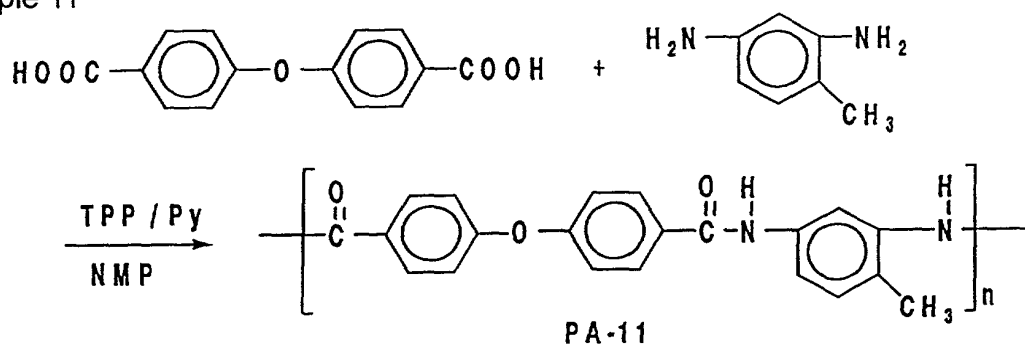
Under argon gas atmosphere, 2.03 g (10.0 mmol) of isophthalic acid dichloride and 2.00 g (10.0 mmol) of 3,4'-diaminodiphenylether were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for one hour at room temperature. Reaction liquid solution thus obtained was diluted with 30 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 3.71 g of polyamide shown in the structural formula PA-9 was obtained. Number-average molecular weight and weight-average molecular weight of PA-9 obtained through the gel permeation chromatography were 1.33×10^4 and 2.59×10^4 , respectively.

Example 10



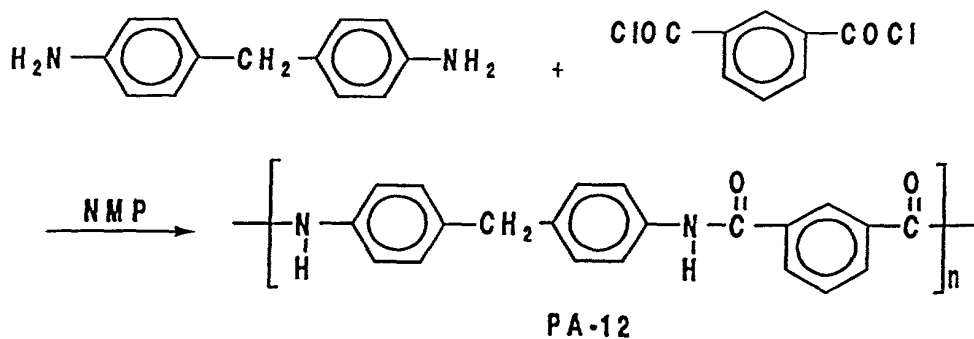
Under flowing nitrogen gas, 1.29 g (5.0 mmol) of 4,4'-dicarboxyphenylether and 0.54 g (5.0 mmol) of m-phenylenediamine were dissolved in 5.55 ml of NMP, and 0.97 ml of Py and 3.14 ml of TPP were added into this liquid solution and stirred for 6 hours after heated to 80°C. Obtained reaction liquid solution was diluted with 14 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 1.72 g of polyamide shown in the structural formula PA-10 above was obtained. Number-average molecular weight and weight-average molecular weight of PA-10 obtained through the gel permeation chromatography were 1.32×10^4 and 2.88×10^4 , respectively.

Example 11



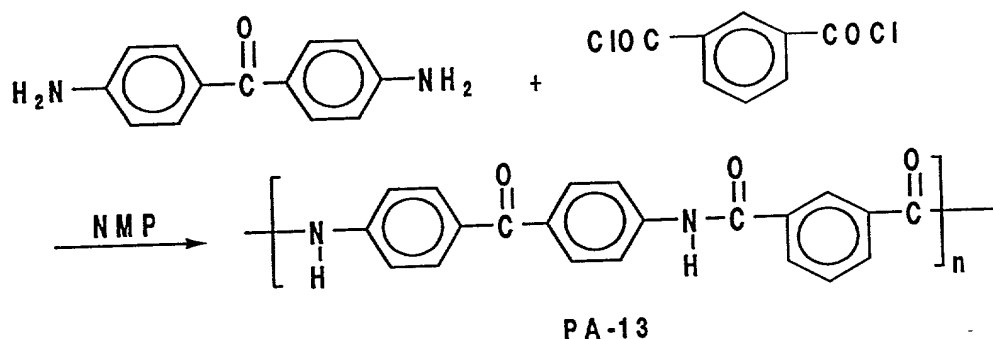
Under flowing nitrogen gas, 1.29 g (5.0 mmol) of 4,4'-dicarboxydiphenylether and 0.61 g (5.0 mmol) of 4-methyl-m-phenylenediamine were dissolved in 6.09 ml of NMP, and 0.97 ml of Py and 3.14 ml of TPP were added into this liquid solution and stirred for 17 hours after heated to 100°C. Obtained reaction liquid solution was diluted with 14.5 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 1.84 g of polyamide shown in the structural formula PA-11 above was obtained. Number-average molecular weight and weight-average molecular weight of PA-11 obtained through the gel permeation chromatography were 1.24×10^4 and 2.47×10^4 , respectively.

Example 12



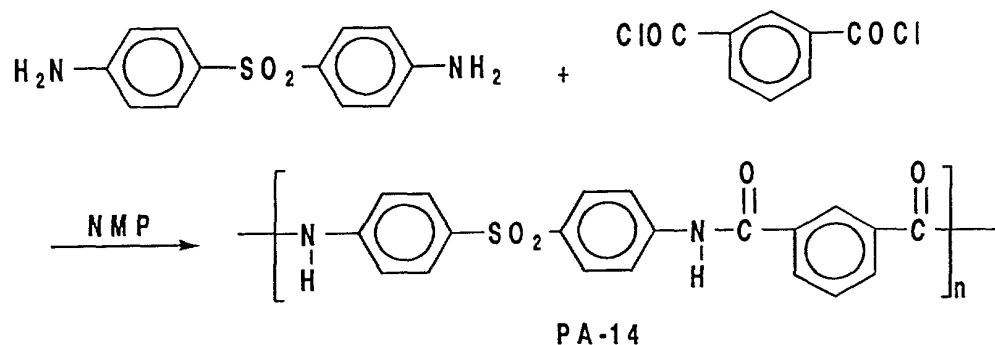
Under argon gas atmosphere, 2.03 g (10.0 mmol) of isophthalic acid dichloride and 1.98 g (10.0 mmol) of 4,4'-diaminodiphenylmethane were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was gradually heated to room temperature to melt and stirred for 30 minutes at room temperature. Reaction liquid solution thus obtained was diluted with 30 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 3.61 g of polyamide shown in the structural formula PA-12 was obtained. Number-average molecular weight and weight-average molecular weight of PA-12 obtained through the gel permeation chromatography were 3.81×10^3 and 5.41×10^3 , respectively.

Example 13



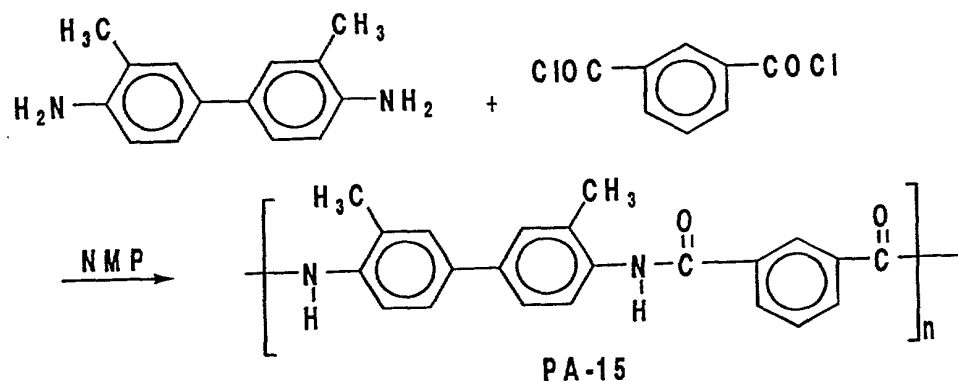
Under argon gas atmosphere, 2.03 g (10.0 mmol) of isophthalic acid dichloride and 2.12 g (10.0 mmol) of 4,4'-diaminobenzophenone were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was gradually heated to room temperature to melt and stirred for 30 minutes at room temperature. Reaction liquid solution thus obtained was diluted with 32 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 3.90 g of polyamide shown in the structural formula PA-13 was obtained. Number-average molecular weight and weight-average molecular weight of PA-13 obtained through the gel permeation chromatography were 3.31×10^3 and 5.55×10^3 , respectively.

Example 14



Under argon gas atmosphere, 2.03 g (10.0 mmol) of isophthalic acid dichloride and 2.48 g (10.0 mmol) of 4,4'-diaminodiphenylsulfone were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was gradually heated to room temperature to melt and stirred for three hours at room temperature. Reaction liquid solution thus obtained was diluted with 35 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 4.19 g of polyamide shown in the structural formula PA-14 was obtained. Number-average molecular weight and weight-average molecular weight of PA-14 obtained through the gel permeation chromatography were 3.98×10^3 and 8.18×10^3 , respectively.

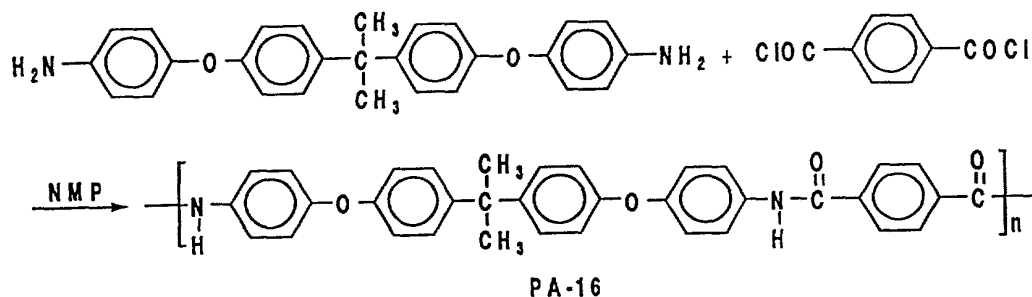
Example 15



Under argon gas atmosphere, 4.06 g (20.0 mmol) of isophthalic acid dichloride and 4.25 g (20.0 mmol) of 3,3'-dimethyl-4,4'-diaminobiphenyl were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and

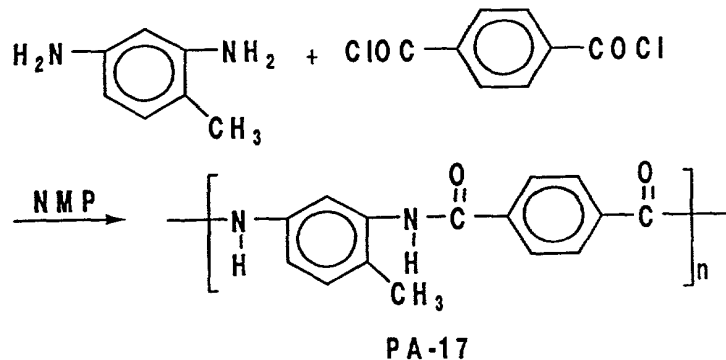
stirred for 30 minutes at room temperature. Reaction liquid solution thus obtained was diluted with 64 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 7.65 g of polyamide shown in the structural formula PA-15 was obtained. Number-average molecular weight and weight-average molecular weight of PA-15 obtained through the gel permeation chromatography were 6.67×10^3 and 1.23×10^4 , respectively.

Example 16



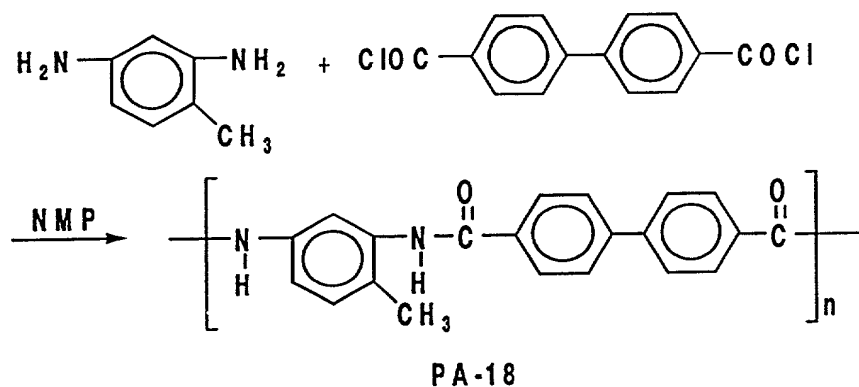
Under argon gas atmosphere, 2.03 g (10.0 mmol) of terephthalic acid dichloride and 4.10 g (10.0 mmol) of 2,2-bis [4-(4-aminophenoxy) phenyl] propane were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for one hour at room temperature. Reaction liquid solution thus obtained was diluted with 47 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 5.58 g of polyamide shown in the structural formula PA-16 was obtained. Number-average molecular weight and weight-average molecular weight of PA-16 obtained through the gel permeation chromatography were 4.42×10^4 and 8.17×10^4 , respectively.

Example 17



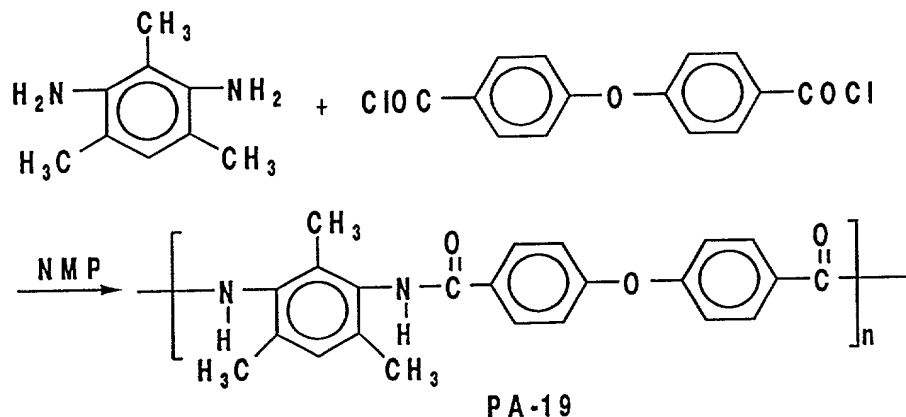
Under argon gas atmosphere, 2.03 g (10.0 mmol) of terephthalic acid dichloride and 1.22 g (10.0 mmol) of 4-methyl-m-phenylenediamine were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for one hour at room temperature. Reaction liquid solution thus obtained was diluted with 25 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 2.99 g of polyamide shown in the structural formula PA-17 was obtained. Number-average molecular weight and weight-average molecular weight of PA-17 obtained through the gel permeation chromatography were 9.33×10^3 and 1.74×10^4 , respectively.

Example 18



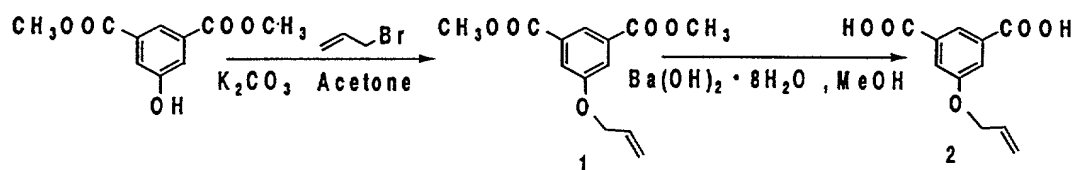
Under argon gas atmosphere, 2.79 g (10.0 mmol) of 4,4'-di (chlorocarbonyl) biphenyl and 1.22 g (10.0 mmol) of 4-methyl-m-phenylenediamine were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for 30 minutes at room temperature. Reaction liquid solution thus obtained was diluted with 30 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 3.73 g of polyamide shown in the structural formula PA-18 was obtained. Number-average molecular weight and weight-average molecular weight of PA-18 obtained through the gel permeation chromatography were 5.04×10^3 and 8.61×10^3 , respectively.

Example 19



Under argon gas atmosphere, 2.95 g (10.0 mmol) of 4,4'-di (chlorocarbonyl) diphenylether and 1.50 g (10.0 mmol) of 2,4,6-trimethyl-m-phenylenediamine were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for one hour at room temperature. Reaction liquid solution thus obtained was diluted with 35 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 3.56 g of polyamide shown in the structural formula PA-19 was obtained. Number-average molecular weight and weight-average molecular weight of PA-19 obtained through the gel permeation chromatography were 9.48×10^3 and 1.55×10^4 , respectively.

Reference 1



2.400 g (11.42 mmol) of dimethyl 5-hydroxyisophthalic acid, 1.4 g (11.6 mmol) of 3-bromopropene and 1.6 g (11.6 mmol) of potassium carbonate were dispersed in 40 ml of acetone and stirred for 15 hours at reflux temperature. The mixture was cooled to room temperature and filtered off insoluble salts after the addition of 150 ml of diethylether. The filtrate was concentrated and purified through the silicagelcolumn chromatography (developing solvent : diethylether/hexane=1/2), 2.612 g of dimethyl 5-allyloxyisophthalic acid in water-white solid powder was obtained (yield : 94.1%).

IR (KBr, cm^{-1}): 2955 (w), 1736 (s), 1595 (w), 1458 (w), 1437 (w), 1341, 1318 (w),

1252 (s), 1115 (w), 1044, 1011 (w), 928 (w), 876 (w), 756.

$^1\text{H-NMR}$ δ (250 MHz, CDCl_3 , ppm) : 3.94 (6H, s), 4.6 (2H, dt), 5.4 (2H, m), 6.0 (1H, m), 7.77 (2H, s), 8.3 (1H, s).

1.109 g (4.432 mmol) of dimethyl 5-allyloxyisophthalic acid obtained in the reaction above was dissolved in 50 ml of methanol, and mixed for 2.5 days at room temperature after the addition of 2.8 g (8.9 mmol) of barium hydroxide (octahydrate). Methanol was distilled off after acidification with 1N hydrochloric acid. Precipitate were washed with water after filtering off and 0.924 g of 5-allyloxyisophthalic acid shown in the structural formula 2 above in water-white powder was obtained on drying (Yield : 93.8%).

IR (KBr, cm^{-1}) : 3100-2500 (br), 1692 (s), 1592, 1462, 1420, 1316, 1277 (s), 1127 (w), 1038, 939, 912, 762, 694.

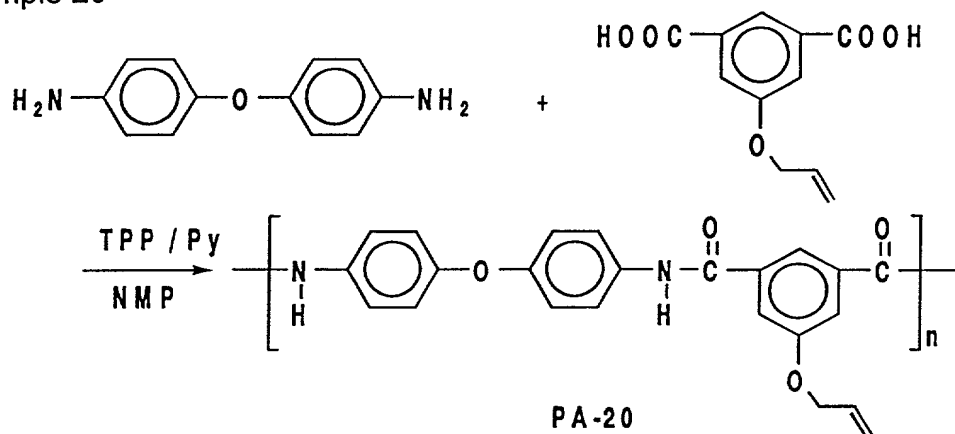
$^1\text{H-NMR}$ δ (500MHz, Acetone- d_6 , ppm) : 4.744 (2H, dt, $J=1.5, 5.1\text{Hz}$), 5.299 (1H, dd, $J=1.5, 10.6\text{Hz}$), 5.474 (1H, dd, $J=1.7, 17.3\text{Hz}$), 6.12 (1H, m), 7.787 (2H, d, $J=1.4\text{Hz}$), 8.285 (1H, t), 11.5 (1H, bs).

Result of elementary analysis : (Molecular formula : $\text{C}_{11}\text{H}_{10}\text{O}_5$,
Molecular weight : 222.20)

Calculated value (%) ; C:59.46, H: 4.54.

Observed value (%) : C: 59.53, H: 4.51.

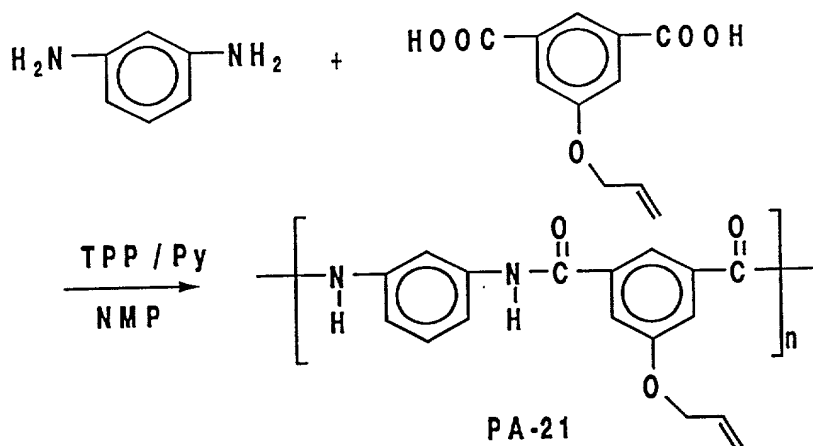
Example 20



Under flowing nitrogen gas, 0.44 g (2.0 mmol) of 5-allyloxyisophthalic acid obtained in Reference 1 above and 0.40 g (2.0 mmol) of 4,4'-diaminodiphenylether were dissolved in 2.84 ml of NMP, and 0.39 ml of Py and 1.26 ml of TPP were added into this liquid solution and stirred for 6 hours after heated to 100°C.

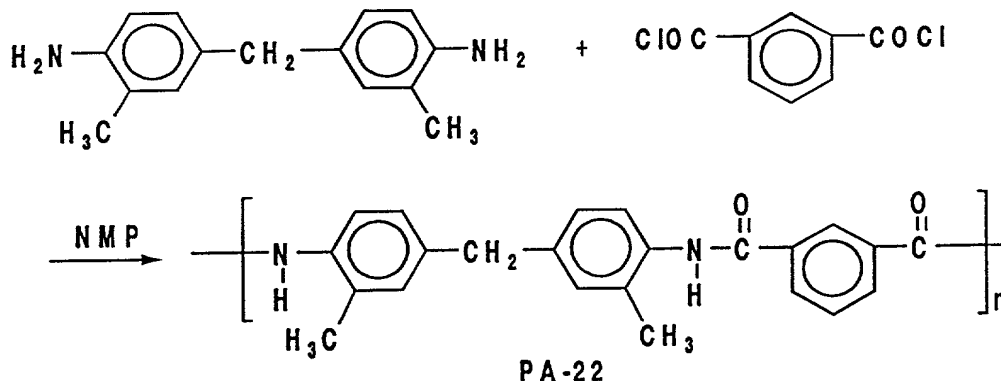
Obtained reaction liquid solution was diluted with 6.4 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 0.80 g of polyamide shown in the structural formula PA-20 above was obtained. Number-average molecular weight and weight-average molecular weight of PA-20 obtained through the gel permeation chromatography were 5.99×10^3 and 1.33×10^4 , respectively.

Example 21



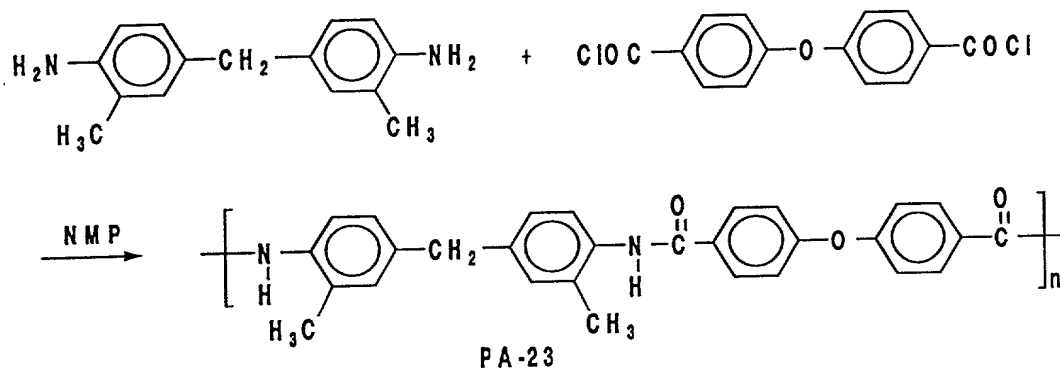
Under flowing nitrogen gas, 0.44 g (2.0 mmol) of 5-allyloxyisophthalic acid obtained in Reference 1 above and 0.22 g (2.0 mmol) of m-phenylenediamine were dissolved in 1.82 ml of NMP, and 0.39 ml of Py and 1.26 ml of TPP were added into this liquid solution and stirred for 6 hours after heated to 100°C. Obtained reaction liquid solution was diluted with 5.0 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 0.64 g of polyamide shown in the structural formula PA-21 above was obtained. Number-average molecular weight and weight-average molecular weight of PA-21 obtained through the gel permeation chromatography were 8.20×10^3 and 1.42×10^4 , respectively.

Example 22



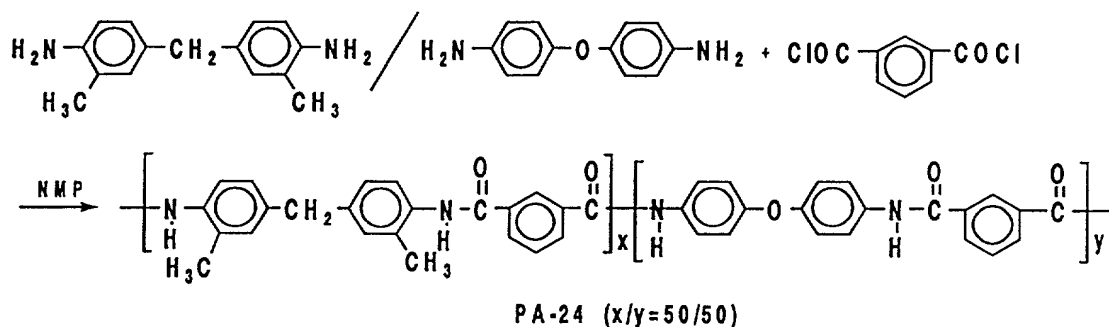
Under argon gas atmosphere, 2.03 g (10.0 mmol) of isophthalic acid dichloride and 2.26 g (10.0 mmol) of 3,3'-dimethyl-4,4'-diaminodiphenylmethane were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for 4 hours at room temperature. Reaction liquid solution thus obtained was diluted with 32 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 3.90 g of polyamide shown in the structural formula PA-22 was obtained. Number-average molecular weight and weight-average molecular weight of PA-22 obtained through the gel permeation chromatography were 1.76×10^4 and 6.71×10^4 , respectively.

Example 23



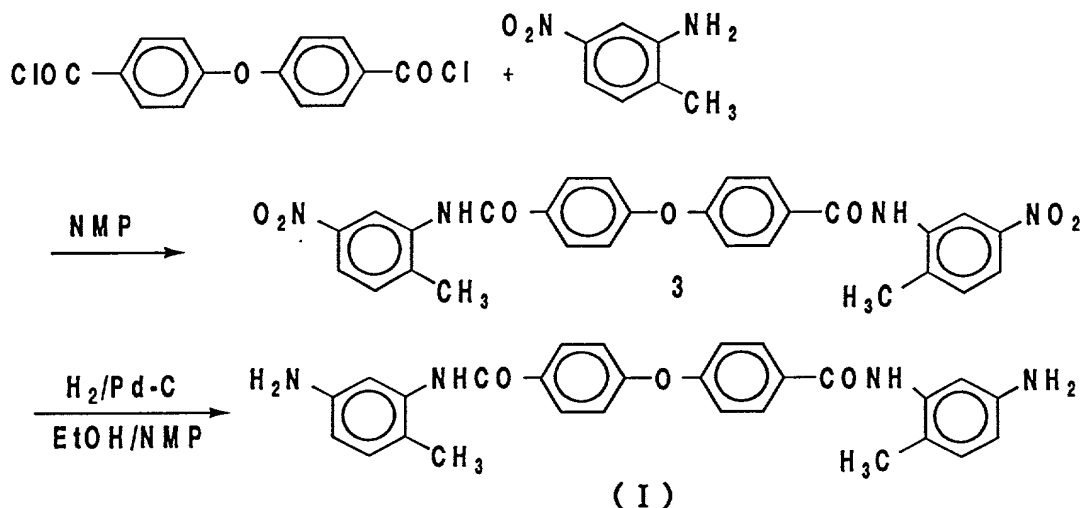
Under argon gas atmosphere, 2.95 g (10.0 mmol) of 4,4'-di (chlorocarbonyl) diphenylether and 2.26 g (10.0 mmol) of 3,3'-dimethyl-4,4'-diaminodiphenylmethane were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for 4 hours at room temperature. Reaction liquid solution thus obtained was diluted with 39 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 4.95 g of polyamide shown in the structural formula PA-23 was obtained. Number-average molecular weight and weight-average molecular weight of PA-23 obtained through the gel permeation chromatography were 1.58×10^4 and 4.01×10^4 , respectively.

Example 24



Under argon gas atmosphere, 2.03 g (10.0 mmol) of isophthalic acid dichloride and 1.13 g (5.0 mmol) of 3,3'-dimethyl-4,4'-diaminodiphenylmethane as well as 1.00 g (5.0 mmol) of 4,4'-diaminodiphenylether were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for 4 hours at room temperature. Reaction liquid solution thus obtained was diluted with 31 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 3.91 g of polyamide shown in the structural formula PA-24 was obtained. Number-average molecular weight and weight-average molecular weight of PA-24 obtained through the gel permeation chromatography were 1.72×10^4 and 4.39×10^4 , respectively.

Reference 2



5.16 g (3.9 mmol) of 2-amino-4-nitrotoluene was dissolved in 10 ml of NMP, and cooled in an ice bath. 5.00 g (16.9 mmol) of 4,4'-di (chlorocarbonyl) diphenylether dissolved in 20 ml of NMP was added to this solution drop-wise over 20 minutes and further stirred for 1.5 hours while bringing back to room temperature. The liquid solution was poured into 500 ml of ice water and precipitate produced were dispersed in the mixed solvent with 20 ml of NMP and 100 ml of ethanol,

washed upon heating and filtered, and 7.38 g of 4,4'-di [N-(2-methyl-5-nitrophenyl) carbonylamino] diphenylether in white powder was obtained (Yield : 82.7%).

IR (KBr, cm^{-1}) : 3274, 1655 (s), 1595, 1524 (s), 1499, 1476 (w), 1350 (s), 1321, 1252 (s), 1170(w), 1076 (w), 1013 (w), 885 (w), 822 (w), 739 (w), 658 (w).

$^1\text{H-NMR}$ δ (500MHz, DMSO-d_6 , ppm) : 2.51 (6H, s), 7.24 (4H, d, $J=8.7\text{Hz}$), 7.58 (2H, d, $J=8.5\text{Hz}$), 8.04 (2H, dd, $J=2.4, 8.4\text{Hz}$), 8.10 (4H, d, $J=8.7\text{Hz}$), 8.35 (2H, d, $J=2.3\text{Hz}$), 10.15 (2H, s).

Result of elementary analysis : (Molecular formula: $\text{C}_{28}\text{H}_{22}\text{O}_7$,
Molecular weight: 526.50)

Calculated value (%) ; C:63.87, H: 4.22, N: 10.64.

Observed value (%) : C: 63.83, H: 4.15, N: 10.56.

3.00 g (5.70 mmol) of 4,4'-di [N-(2-methyl-5-nitrophenyl) carbonylamino] diphenylether obtained in the reaction above was dissolved into the solvent mixture with 50 ml of ethanol and 80 ml of NMP, and then 0.240 g of 5%Pd carbon powder were dispersed. The mixture was thoroughly deaerated under the reduced pressure at -78°C , and then stirred for 6.5 hours after the system was replaced with hydrogen gas and temperature was brought back to room temperature. Precipitate obtained after removing catalyst with Celite and removing solvent by distillation under the reduced pressure was dispersed in 50 ml of ethanol, washed upon heating at 80°C and filtered, 2.50 g of 4,4'-di [N-(2-methyl-5-aminophenyl) carbonylamino] diphenylether shown in the structural formula (I) above in white powder was obtained (Yield : 94.0%).

IR (KBr, cm^{-1}) : 3427, 3345, 3275 (br), 1655 (s), 1601, 1586, 1543 (s), 1505 (s), 1493, 1454, 1327 (w), 1281, 1258 (s), 1169, 1107 (w), 1011 (w), 897 (w), 856 (w), 843, 681.

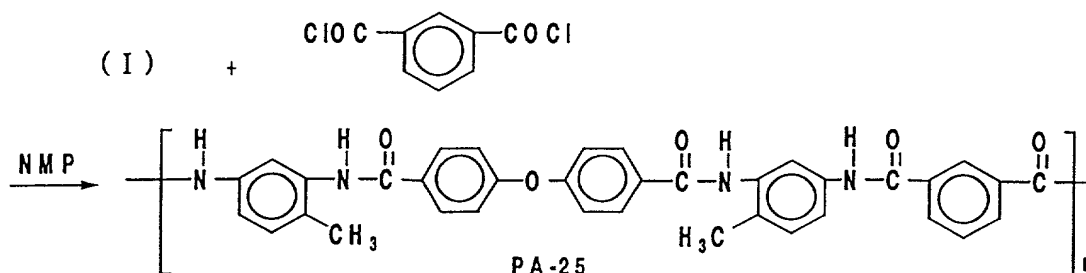
$^1\text{H-NMR}$ δ (500MHz, DMSO-d_6 , ppm) : 2.06 (6H, s), 4.90 (4H, s), 6.40 (2H, dd, $J=2.2, 8.1\text{Hz}$), 6.60 (2H, d, $J=2.1\text{Hz}$), 6.88 (2H, d, $J=8.1\text{Hz}$), 7.17 (4H, d, $J=8.7\text{Hz}$), 8.03 (4H, d, $J=8.7\text{Hz}$), 9.63 (2H, s).

Result of elementary analysis : (Molecular formula: $\text{C}_{28}\text{H}_{26}\text{N}_4\text{O}_3$,
Molecular weight: 466.53)

Calculated value (%) ; C:69.68, H: 6.28, N: 17.41.

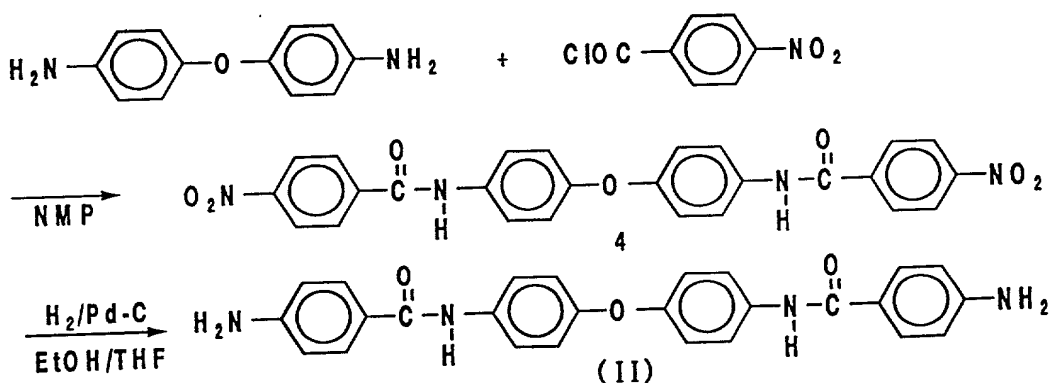
Observed value (%) : C: 69.90, H: 6.40, N: 17.14.

Experiment 25.



Under argon gas atmosphere, 1.02 g (5.0 mmol) of isophthalic acid dichloride and 2.33 g (5.0 mmol) of 4,4'-di [N-(2-methyl-5-aminophenyl) carbonylamino] diphenylether obtained in Reference 2 above were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for 4 hours at room temperature. Reaction liquid solution thus obtained was diluted with 25.0 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 3.15 g of polyamide shown in the structural formula PA-25 was obtained. Number-average molecular weight and weight-average molecular weight of PA-25 obtained through the gel permeation chromatography were 1.61×10^4 and 3.05×10^4 , respectively.

Reference 3



5.00 g (25.0 mmol) of 4,4'-diaminodiphenylether was dissolved in 30 ml of NMP and cooled in an ice bath. 9.78 g (52.7 mmol) of 4-nitrobenzoic acid in 30 ml of NMP was added to the solution by drop-wise over one hour and stirred for two

hours while bringing back to room temperature. The solution was poured into 500 ml of ice water and the precipitate produced was recovered and washed thoroughly with water. The precipitate in the solvent mixture of acetic acid/THF was purified by recrystallization, 11.63 g of 4,4'-di (4-nitrobenzamide) diphenylether shown in the structural formula 4 above was obtained in white powder (Yield :93.4%).

IR (KBr, cm^{-1}) : 3360, 2924, 1649 (s), 1603 (s), 1539 (s), 1507 (s), 1408 (w), 1350, 1327, 1253, 1225, 1096 (w), 1015 (w), 870, 853, 826, 698 (w).

$^1\text{H-NMR}$ δ (500MHz, DMSO-d_6 , ppm) : 7.06 (4H, d, $J=8.9\text{Hz}$), 7.80 (4H, d, $J=8.9$), 8.19 (4H, d, $J=8.8\text{Hz}$), 8.38 (4H, d, $J=8.8\text{Hz}$), 10.61 (2H, s).

Result of elementary analysis : (Molecular formula: $\text{C}_{26}\text{H}_{18}\text{N}_4\text{O}_7$,
Molecular weight: 498.45)

Calculated value (%) ; C:62.65, H: 3.65, N: 12.84.

Observed value (%) : C: 62.60, H: 3.54, N: 12.19.

3.50 g (7.02 mmol) of 4,4'-di (4-nitrobenzamide) diphenylether was dissolved in the solvent mixture with 100 ml ethanol and 300 ml of THF, and 0.38 g of 5% Pd-carbon powder was dispersed into this solution. The solution was thoroughly deaerated under the reduced pressure at -78°C , and then stirred for 18 hours after the system was replaced with hydrogen gas and temperature was brought back to room temperature. The precipitate obtained after removing catalyst with Celite and removing solvent by the distillation under the reduced pressure was purified by re-crystallization after dissolving in the solvent mixture of ethanol/THF, 2.98 g of 4,4'-di (4-aminobenzamide) diphenylether shown in the structural formula (II) above was obtained in white powder (Yield :96.8%).

IR (KBr, cm^{-1}) : 3440, 3347, 3288 (br), 3210, 1609 (s), 1570 (w), 1501 (s), 1406, 1310, 1269, 1223 (s), 1182, 876 (w), 841, 766 (w), 689 (w).

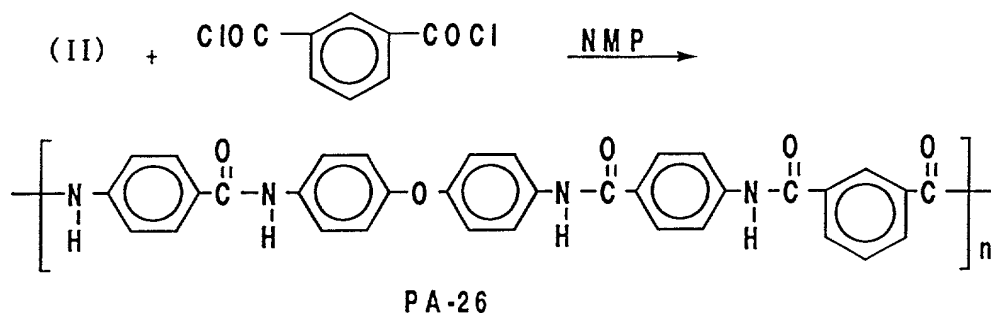
$^1\text{H NMR}$ δ (500MHz, DMSO-d_6 , ppm) : 5.73 (4H, s), 6.59 (4H, d, $J=8.6\text{Hz}$), 6.96 (4H, d, $J=9.0\text{Hz}$), 7.72 (8H, m), 9.76 (2H, s).

Result of elementary analysis : (Molecular formula: $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_3$,
Molecular weight: 438.48)

Calculated value (%) ; C:71.21, H: 5.07, N: 14.60.

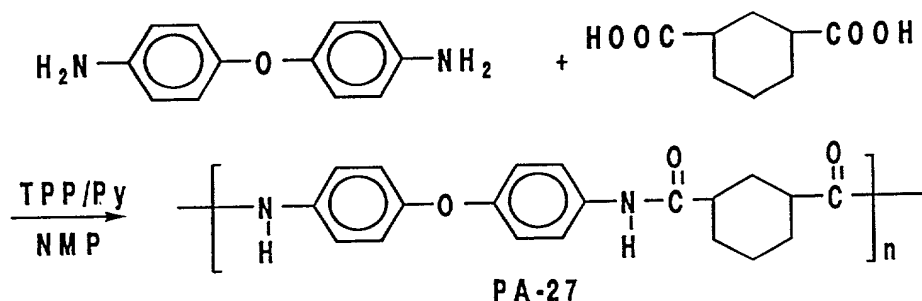
Observed value (%) : C: 71.01, H: 5.24, N: 14.33.

Example 26



Under argon gas atmosphere, 1.02 g (5.0 mmol) of isophthalic acid dichloride and 2.19 g (5.0 mmol) of 4,4'-di (4-aminobenzamide) diphenylether obtained in Reference 3 shown in the formula (II) above were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for 4 hours at room temperature. Reaction liquid solution thus obtained was diluted with 24.0 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 2.92 g of polyamide shown in the structural formula PA-26 was obtained. Number-average molecular weight and weight-average molecular weight of PA-26 obtained through the gel permeation chromatography were 1.91×10^4 and 4.08×10^4 , respectively.

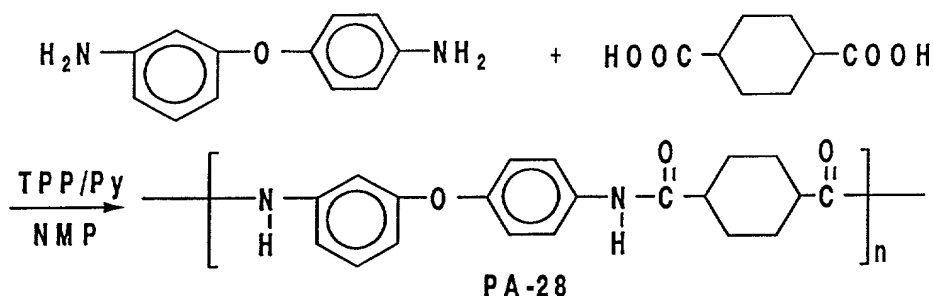
Example 27



Under flowing nitrogen gas, 1.72 g (10.0 mmol) of 1,3-dicarboxycyclohexane and 2.00 g (10.0 mmol) of 4,4'-diaminodiphenylether were dissolved in 24.67 ml of NMP, and 3.56 ml of Py and 7.45 ml of TPP were added into this liquid solution and stirred for 6 hours after heated to 80°C . Obtained reaction liquid solution was diluted with 28 ml of NMP and then poured into excess methanol, and polymer

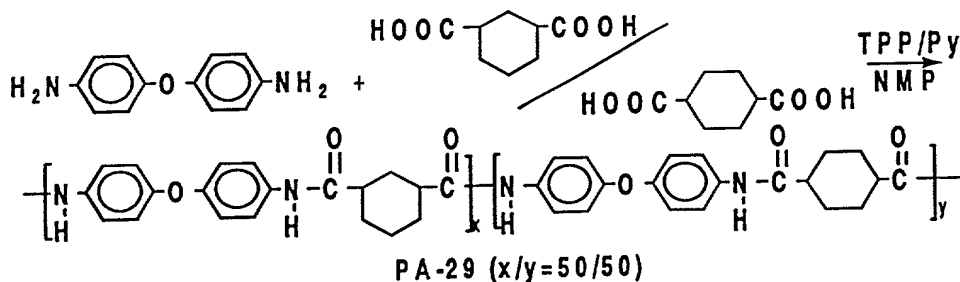
precipitated were filtered and dried. The procedures above were repeated and purified, and 3.15 g of polyamide shown in the structural formula PA-27 above was obtained. Number-average molecular weight and weight-average molecular weight of PA-27 obtained through the gel permeation chromatography were 4.45×10^4 and 8.23×10^4 , respectively.

Example 28



Under flowing nitrogen, 1.72 g (10.0 mmol) of 1,4-dicarboxycyclohexane and 2.00 g (10.0 mmol) of 3,4'-diaminodiphenylether were dissolved in 24.67 ml of NMP, and 3.56 ml of Py and 7.45 ml of TPP were added into this liquid solution and stirred for 6 hours after heated to 80°C. Obtained reaction liquid solution was diluted with 28 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 3.05 g of polyamide shown in the structural formula PA-28 above was obtained. Number-average molecular weight and weight-average molecular weight of PA-28 obtained through the gel permeation chromatography were 2.14×10^4 and 4.35×10^4 , respectively.

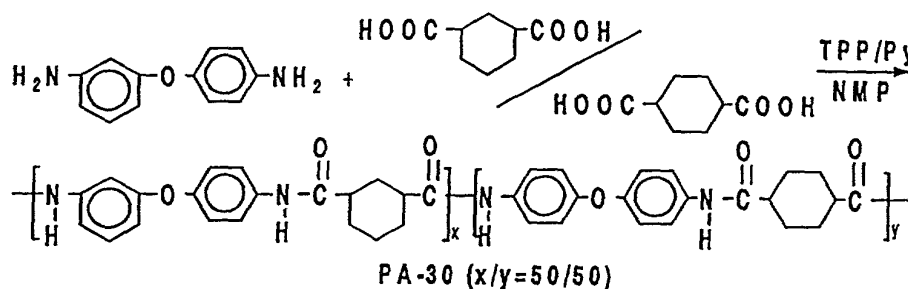
Example 29



Under flowing nitrogen gas, 0.86 g (5.0 mmol) of 1,3-dicarboxycyclohexane and 0.86g (5.0 mmol) of 1,4-dicarboxylcyclohexane as well as 2.00 g (10.0 mmol) of

4,4'-diaminodiphenylether were dissolved in 24.67 ml of NMP, and 3.56 ml of Py and 7.45 ml of TPP were added into this liquid solution and stirred for 6 hours after heated to 80°C. Obtained reaction liquid solution was diluted with 28 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 2.98 g of polyamide shown in the structural formula PA-29 above was obtained. Number-average molecular weight and weight-average molecular weight of PA-29 obtained through the gel permeation chromatography were 3.76×10^4 and 5.96×10^4 , respectively.

Example 30



Under flowing nitrogen gas, 0.86 g (5.0 mmol) of 1,3-dicarboxycyclohexane and 0.86g (5.0 mmol) of 1,4-dicarboxycyclohexane as well as 2.00 g (10.0 mmol) of 3,4'-diaminodiphenylether were dissolved in 24.67 ml of NMP, and 3.56 ml of Py and 7.45 ml of TPP were added into this liquid solution and stirred for 6 hours after heated to 80°C. Obtained reaction liquid solution was diluted with 28 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 2.79 g of polyamide shown in the structural formula PA-30 above was obtained. Number-average molecular weight and weight-average molecular weight of PA-30 obtained through the gel permeation chromatography were 1.87×10^4 and 4.64×10^4 , respectively.

Example 31

Under argon gas atmosphere, 0.30 g of PA-1 obtained in Example 1 was dissolved in 6 ml of dimethylsulfoxide (abbreviated as DMSO hereafter), and 2 ml of 1N potassium hydroxide/methanol solution was added to this solution and stirred for one hour at room temperature. The solution was then stirred for additional 30 minutes at room temperature after the addition of 0.4 ml of iodomethane. The reaction solution thus obtained was poured into excess methanol, and polymer precipitated were filtered and dried to yield 0.27 g of polymer. ¹H-NMR spectrum of polymer obtained was taken and revealed that the product was polyamide (called PA-31 hereafter) in which 31 mole % of amide radical at N position of the structure shown in PA-1 was substituted with methyl group. Number-average molecular

weight and weight-average molecular weight of PA-31 obtained through the gel permeation chromatography were 1.43×10^4 and 2.96×10^4 , respectively.

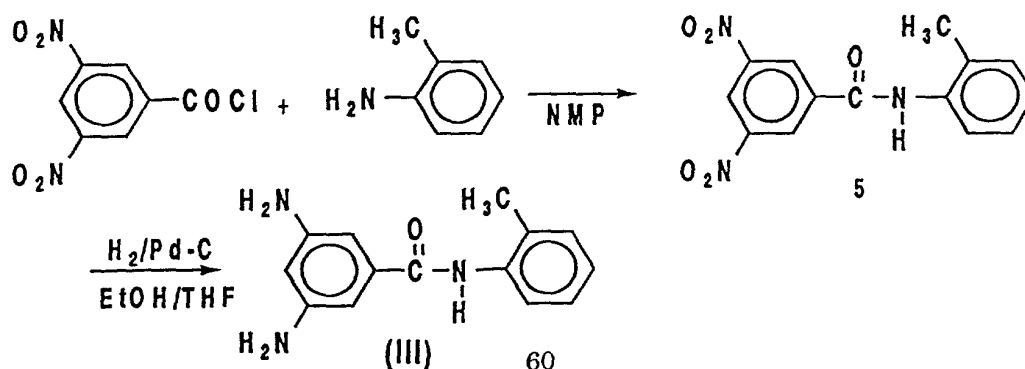
Example 32

Under argon gas atmosphere, 0.80 g of PA-6 obtained in Example 6 was dissolved in 13 ml of DMSO, and 7 ml of 1N potassium hydroxide/methanol solution was added to this solution and mixed for one hour at room temperature. The solution was then stirred for additional 30 minutes at room temperature after the addition of 1.2 ml of iodomethane. The reaction solution thus obtained was poured into excess methanol, and polymer precipitated were filtered and dried to yield 0.88 g of polymer. $^1\text{H-NMR}$ spectrum of polymer obtained was taken and revealed that the product was polyamide (called PA-32 hereafter) in which 24 mole % of amide radical at N position of the structure shown in PA-6 was substituted with methyl group. Number-average molecular weight and weight-average molecular weight of PA-32 obtained through the gel permeation chromatography were 5.63×10^3 and 8.47×10^3 , respectively.

Example 33

Under argon gas atmosphere, 110 mg (2.75 mmol) of sodium hydride (oil, 60%) was dispersed in 20 ml of DMSO and light yellow homogeneous solution was obtained after stirring the solution for one hour at 70°C . 0.86 g of polyamide PA-6 obtained in Example 6 was dissolved in the solution and stirred for additional 4 hours at room temperature. The solution was then stirred for additional 15 hours at room temperature after the addition of 0.5 ml of iodomethane (8.03 mmol), the reaction solution thus obtained was poured into excess methanol, and polymer precipitated were filtered and dried to yield 0.69 g of polymer. $^1\text{H-NMR}$ spectrum of polymer obtained was taken and revealed that the product was polyamide (called PA-33 hereafter) in which 37 mole % of amide radical at N position of the structure shown in PA-6 was substituted with methyl group. Number-average molecular weight and weight-average molecular weight of PA-33 obtained through the gel permeation chromatography were 6.21×10^3 and 9.34×10^3 , respectively.

Reference 4



4.788 g (44.68 mmol) of 2-aminotoluene was dissolved in 14 ml of NMP and cooled in an ice bath. 10.396 g (45.10 mmol) of 3,5-dinitro benzoic acid chloride in 30 ml of NMP solution was added to the solution drop-wise over 20 minutes and stirred for additional one hour while bringing back to room temperature. The solution was poured into 500 ml of water and precipitate produced was recovered and washed thoroughly with water. The precipitate in the solvent mixture of chloroform/THF was purified by re-crystallization, and 10.20 g of 3,5-dinitro-2'-methylbenzanilide shown in the structural formula 5 above was obtained in yellow needle shaped crystal (Yield :75.8%).

IR (KBr, cm^{-1}) : 3256, 3104, 1649 (s), 1586 (w), 1537 (s), 1491 (w), 1456, 1343 (s), 1312, 1275, 1165 (w), 1076, 914, 762, 729, 706.

$^1\text{H-NMR}$ δ (500MHz, DMSO-d_6 , ppm) : 2.26 (3H, s), 7.25 (2H, m), 7.34 (2H, m), 9.02 (1H, t, $J=2.0\text{Hz}$), 9.17 (2H, d, $J=1.9\text{Hz}$), 10.61 (1H, s).

Result of elementary analysis : (Molecular formula: $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_5$,
Molecular weight: 301.25)

Calculated value (%) ; C:55.81, H: 3.69, N: 13.94.

Observed value (%) : C: 55.94, H: 3.53, N: 13.83.

7.00 g (23.3 mmol) of 3,5-dinitro-2'-methylbenzanilide obtained in the reaction above was dissolved in the solvent mixture with 200 ml ethanol and 150 ml of THF, and 0.938 g of 5% Pd-carbon powder was dispersed in this solution. The solution was thoroughly deaerated under the reduced pressure at -78°C , and then stirred for 17 hours after the system was replaced with hydrogen gas and temperature was brought back to room temperature. Precipitate obtained after removing catalyst with Celite and concentrating was dispersed in ethyl acetate, washed and filtered, and 5.52 g of 3,5-diamino-2'-methylbenzanilide shown in the structural formula (III) above in white powder was obtained (Yield :98.4%).

IR (KBr, cm^{-1}) : 3455, 3401, 3328 (s), 3237 (br), 2924 (s), 2855, 1634 (s), 1593 (s), 1512 (s), 1491 (s), 1368, 1273, 1198, 1117 (w), 992 (w), 839, 758, 683, 610.

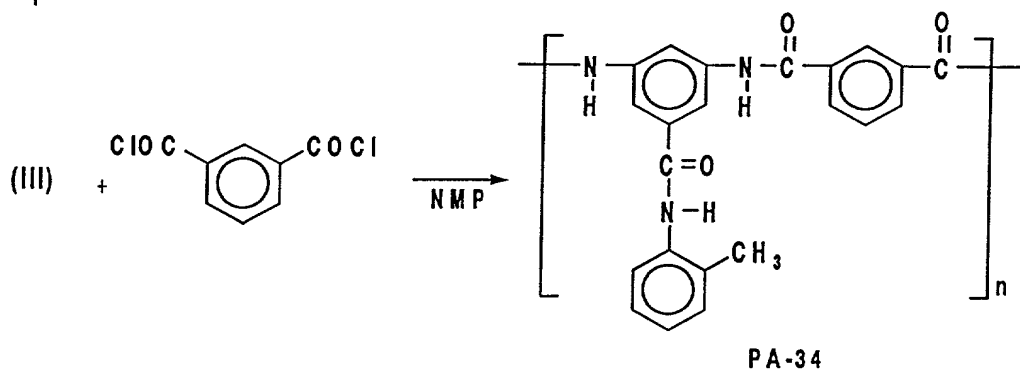
$^1\text{H-NMR}$ δ (500MHz, DMSO-d_6 , ppm) : 2.21 (3H, s), 4.91 (2H, s), 5.99(1H, t, $J=1.9\text{Hz}$), 6.33 (2H, d, $J=1.9\text{Hz}$), 7.11 (1H, m), 7.18 (1H, m), 7.23 (1H, d, $J=7.4\text{Hz}$), 7.32 (1H, d, $J=7.3\text{Hz}$), 9.40(1H, s).

Result of elementary analysis : (Molecular formula: $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}$,
Molecular weight: 241.29)

Calculated value (%) ; C:69.68, H: 6.28, N: 17.41.

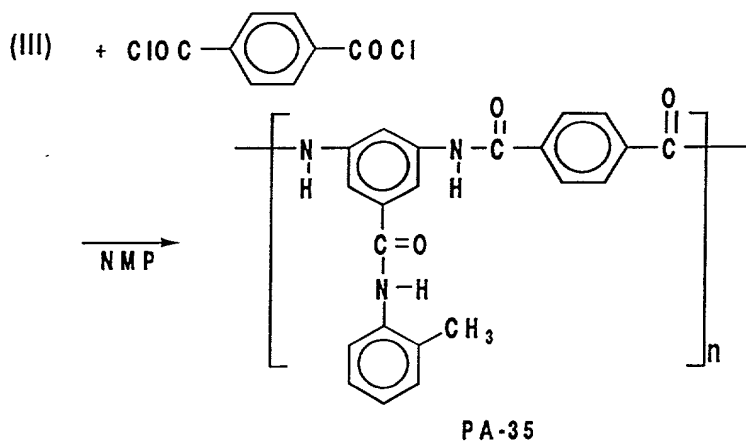
Observed value (%) : C: 69.69, H: 6.41, N: 16.99.

Example 34



Under argon gas atmosphere, 1.02 g (5.0 mmol) of isophthalic acid dichloride and 1.20 g (5.0 mmol) of 3,5-diamino-2'-methylbenzanilide obtained in Reference 4 shown in the formula (III) above were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for 4 hours at room temperature. Reaction liquid solution thus obtained was diluted with 17 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 2.11 g of polyamide shown in the structural formula PA-34 was obtained. Number-average molecular weight and weight-average molecular weight of PA-34 obtained through the gel permeation chromatography were 2.43×10^4 and 4.45×10^4 , respectively.

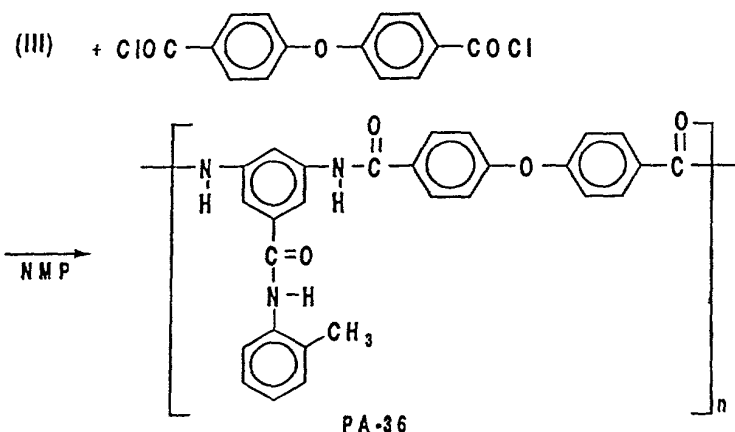
Example 35



Under argon gas atmosphere, 1.02 g (5.0 mmol) of terephthalic acid dichloride and 1.20 g (5.0 mmol) of 3,5-diamino-2'-methylbenzanilide obtained in Reference 4 shown in the formula (III) above were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for one hour at room

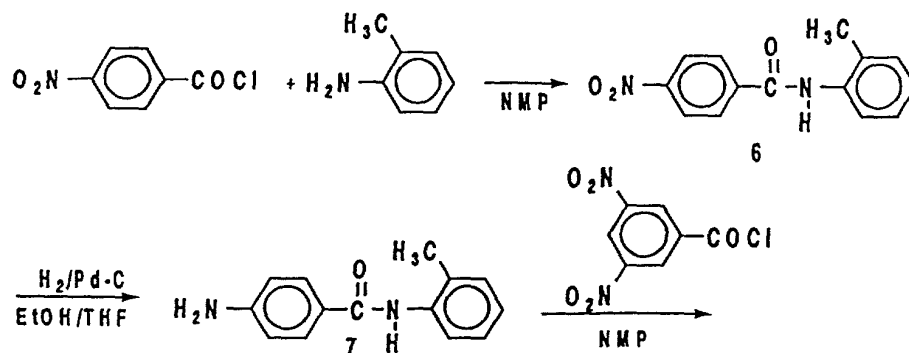
temperature. Reaction liquid solution thus obtained was diluted with 17 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 2.15 g of polyamide shown in the structural formula PA-35 was obtained. Number-average molecular weight and weight-average molecular weight of PA-35 obtained through the gel permeation chromatography were 1.57×10^4 and 3.63×10^4 , respectively.

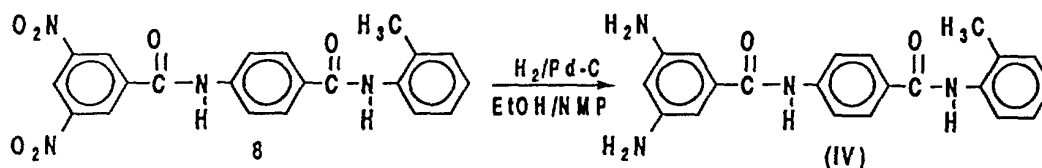
Example 36



Under argon gas atmosphere, 1.48 g (5.0 mmol) of 4,4'-di (chlorocarbonyl) diphenylether and 1.20 g (5.0 mmol) of 3,5-diamino-2'-methylbenzanilide obtained in Reference 4 shown in the formula (III) above were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for one hour at room temperature. Reaction liquid solution thus obtained was diluted with 19 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 2.63 g of polyamide shown in the structural formula PA-36 was obtained. Number-average molecular weight and weight-average molecular weight of PA-36 obtained through the gel permeation chromatography were 2.24×10^4 and 4.28×10^4 , respectively.

Reference 5





1.743 g (16.10 mmol) of 2-aminotoluene was dissolved in 6 ml of NMP and cooled in an ice bath. 3.019 g (16.27 mmol) of 4-nitrobenzoic acid chloride in 10 ml of NMP solution was added to the solution drop-wise over 5 minutes and stirred for additional 30 minutes while bringing back to room temperature. The solution was poured into 500 ml of water and precipitate produced was recovered and washed thoroughly with water. The dried precipitate was purified through the silica gel chromatography (developing solvent : chloroform) and then re-crystallized from the solvent mixture of chloroform/hexane, and 3.604 g of 4-nitro-2'-methylbenzanilide shown in the structural formula 6 above was obtained in yellow needle shaped crystal (Yield :87.4%).

IR (KBr, cm^{-1}) : 3304, 1649, 1603 (w), 1586 (w), 1520 (s), 1454, 1343, 1308, 1109 (w), 856 (w), 841 (w), 758, 710 (w).

$^1\text{H-NMR}$ δ (250MHz, CDCl_3 , ppm) : 2.35 (3H, s), 7.18 (1H, m), 7.29 (2H, m), 7.7 (1H, bs), 7.9 (1H, bd), 8.05 (2H, d), 8.36 (2H, d).

3.00 g (11.7 mmol) of 4-nitro-2'-methylbenzanilide obtained in the reaction above was dissolved in the solvent mixture with 20 ml ethanol and 20 ml of THF, and 0.25 g of 5% Pd-carbon powder was dispersed in this solution. The solution was thoroughly deaerated under the reduced pressure at -78°C , and then stirred for 18 hours after the system was replaced with hydrogen gas and temperature was brought back to room temperature. Precipitate obtained after removing catalyst with Celite and concentrating yielded 2.51 g of 4-amino-2'-methylbenzanilide shown in the structural formula 7 above in light brown solid (Yield :95.5%).

IR (KBr, cm^{-1}) : 3476 (w), 3349, 3289 (w), 1624 (s), 1603, 1568 (w), 1526 (w), 1501 (s), 1453 (w), 1292, 1271, 1182, 843 (w), 747, 588 (w).

$^1\text{H-NMR}$ δ (250MHz, CDCl_3 , ppm) : 2.33 (3H, s), 4.03 (2H, bs), 6.71 (2H, d), 7.1 (1H, m), 7.2 (2H, m), 7.6 (1H, bs), 7.72 (2H, d), 7.95 (1H, d).

4.76 g (21.0 mmol) of 4-amino-2'-methylbenzanilide obtained above was dissolved in 20 ml of NMP and cooled in an ice bath. 4.86 g (21.1 mmol) of 3,5-dinitro benzoic acid chloride in 10 ml of NMP solution was added to the solution drop-wise. The solution was stirred for 30 minutes while bringing back to room

temperature and then poured into 800 ml of ice water. Precipitate produced was recovered by filtration and washed thoroughly with water, and dispersed in 600 ml of sodium hydrogen carbonate solution. Again precipitate was filtered and washed thoroughly. The precipitate obtained was dispersed in the solvent mixture with 50 ml of NMP and 150 ml of ethanol, washed by heating and filtered, and 7.30 g of 3,5-dinitro-4'-[N-(2-methylphenyl) carbamoyl] benzanilide shown in the structural formula 8 above were obtained in white powder (Yield :82.3%).

IR (KBr, cm^{-1}) : 3461, 3308, 3090 (w), 1684, 1651 (s), 1597, 1535 (s), 1454, 1400 (w), 1345, 1319, 1273, 1190 (w), 916 (w), 858 (w), 764, 731, 588 (w).

$^1\text{H-NMR}$ δ (500MHz, DMSO-d_6 , ppm) : 2.26 (3H, s), 7.12 (1H, m), 7.22 (1H, m), 7.28 (1H, d, $J=7.3\text{Hz}$), 7.36 (1H, t, $J=7.3\text{Hz}$), 7.95 (2H, d, $J=8.7\text{Hz}$), 8.05 (2H, d, $J=8.7\text{Hz}$), 9.04 (1H, t, $J=2.1\text{Hz}$), 9.21 (2H, d, $J=2.0\text{Hz}$), 9.84 (1H, s), 11.07 (1H, s).

Result of elementary analysis : (Molecular formula: $\text{C}_{21}\text{H}_{16}\text{N}_4\text{O}_6$,
Molecular weight: 420.38)

Calculated value (%) ; C:59.99, H: 3.84, N: 13.32.

Observed value (%) : C:59.85, H:3.73, N:13.27

5.00 g (11.9 mmol) of 3,5-dinitro-4'-[N-(2-methylphenyl) carbamoyl] benzanilide obtained in the reaction above was dissolved in the solvent mixture with 100 ml ethanol and 200 ml of NMP, and 0.500 g of 5% Pd-carbon powder was dispersed in this solution. The solution was thoroughly deaerated under the reduced pressure at -78°C , and then stirred for 6 hours after the system was replaced with hydrogen gas and temperature was brought back to room temperature. Precipitate obtained after removing catalyst with Celite and removing solvent by distillation under the reduced pressure was dispersed in the solvent mixture with 50 ml of ethyl acetate and 150 ml of ethanol, washed and filtered, and 4.03 g of 3,5-diamino-4'-[N-(2-methylphenyl) carbamoyl] benzanilide shown in the structural formula (IV) above was obtained in white powder (Yield :94.0%).

IR (KBr, cm^{-1}) : 3410, 3324 (br), 3218, 1645 (s), 1591 (s), 1518 (s), 1460, 1402, 1362, 1318, 1252, 1192 (w), 853, 750, 689 (w).

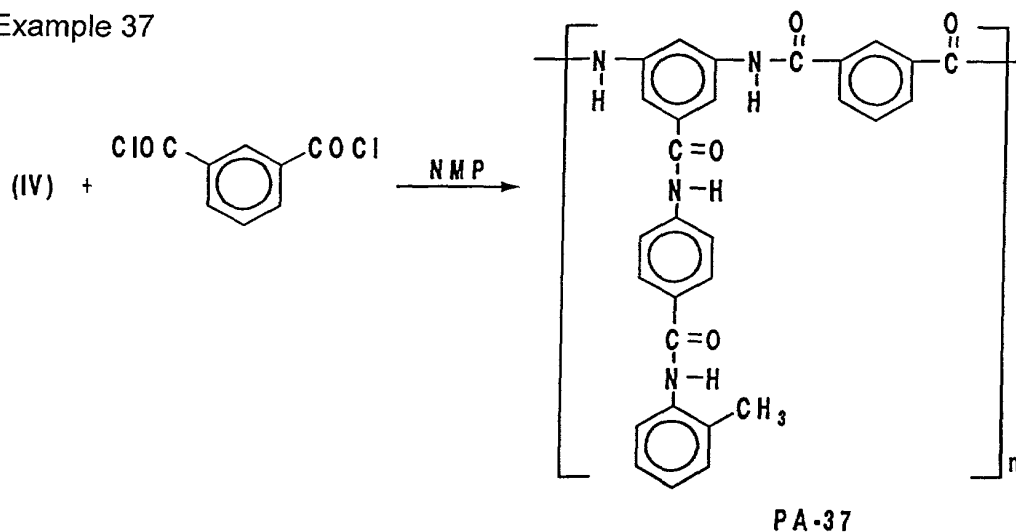
$^1\text{H-NMR}$ δ (500MHz, DMSO-d_6 , ppm) : 2.24 (3H, s), 4.95 (4H, s), 6.02 (1H, t, $J=1.9\text{Hz}$), 6.32 (2H, d, $J=1.9\text{Hz}$), 7.15 (1H, m), 7.21 (1H, m), 7.26 (1H, d, $J=7.2\text{Hz}$), 7.34 (1H, d, $J=7.3\text{Hz}$), 7.89 (2H, d, $J=8.8\text{Hz}$), 7.95 (2H, d, $J=8.8\text{Hz}$), 9.72 (1H, s), 10.19 (1H, s).

Result of elementary analysis : (Molecular formula: $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_2$,
Molecular weight: 360.41)

Calculated value (%) ; C:69.98, H: 5.59, N: 15.54.

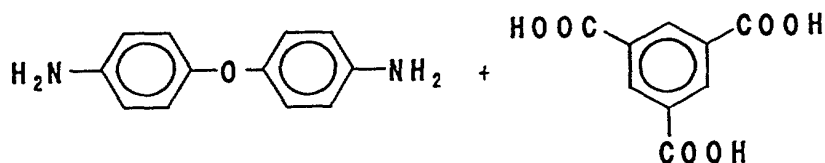
Observed value (%) : C:69.47, H:5.66, N:15.36.

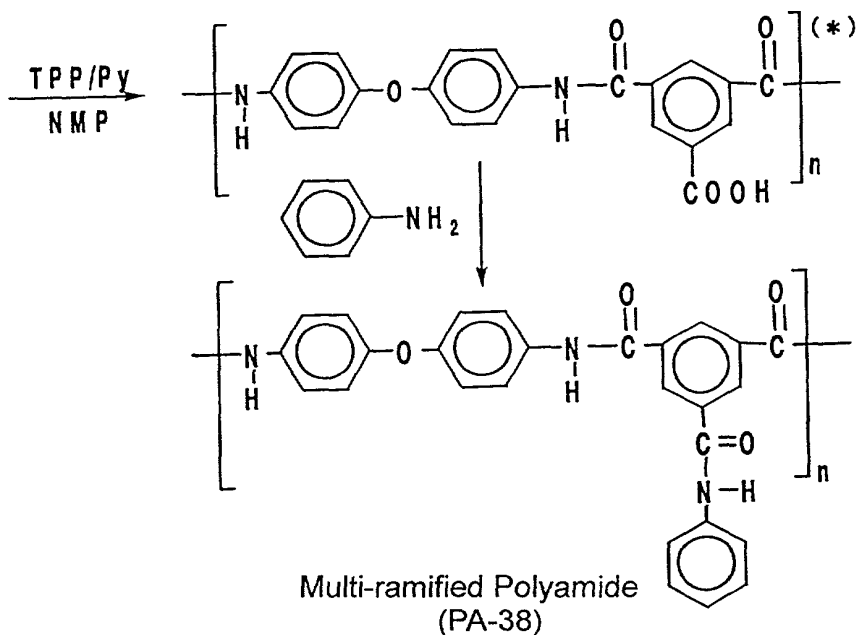
Example 37



Under argon gas atmosphere, 1.02 g (5.0 mmol) of isophthalic acid dichloride and 1.80 g (5.0 mmol) of 3,5-diamino-4'-[N-(2methylphenyl) carbamoyl] benzanilide obtained in Reference 5 shown in the formula (IV) above were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to melt and stirred for 4 hours at room temperature. Reaction liquid solution thus obtained was diluted with 21.0 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 1.24 g of polyamide shown in the structural formula PA-37 was obtained. Number-average molecular weight and weight-average molecular weight of PA-37 obtained through the gel permeation chromatography were 5.44×10^3 and 9.69×10^3 , respectively.

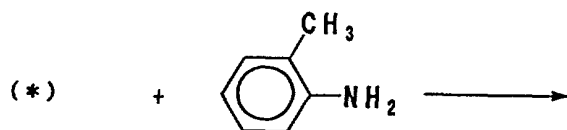
Example 38

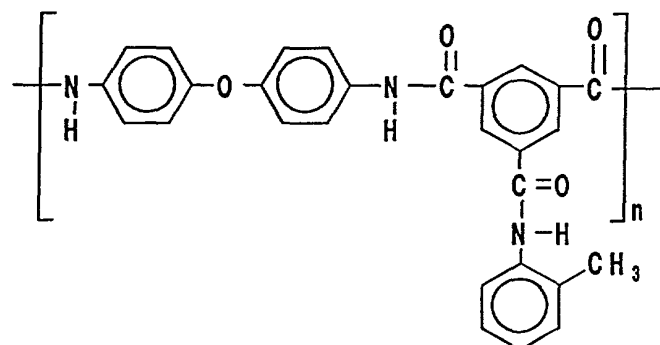




Under argon gas atmosphere, 1.05 g (5.0 mmol) of trimesic acid and 1.00 g (5.0 mmol) of 4,4'-diaminodiphenylether were dissolved in 50 ml of NMP, and 6.0 ml of Py and 8.0 ml of TPP were added into this liquid solution and stirred for 4 hours after heated to 80°C. Polyamide (*) shown in the structural formula above can be obtained by these processes ((* the structure above was shown in this way for convenience, but they have in fact multi-ramified structure). 0.5 g of aniline was then added to the reaction solution and stirred for additional 13 hours at 80°C. Reaction solution thus obtained was poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 2.15 g of multi-ramified type polyamide shown in the structural formula PA-38 (the structure above was shown in this way for convenience, but they have in fact multi-ramified structure) above was obtained. Number-average molecular weight and weight-average molecular weight of PA-38 obtained through the gel permeation chromatography were 1.94×10^4 and 1.96×10^5 , respectively.

Example 39

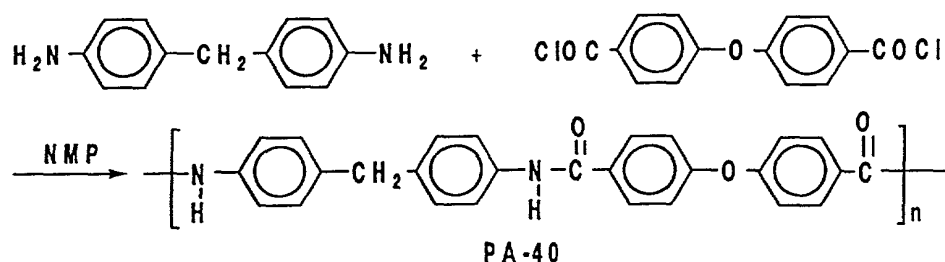




Multi-ramified Polyamide
(PA-39)

0.6 g of o-tolidine was added to the reaction solution of multi-ramified polyamide (*) obtained by the similar procedure as in Example 38 and stirred for 14 hours at 80°C. Reaction solution thus obtained was poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 2.07 g of multi-ramified type polyamide shown in the structural formula PA-39 (the structure above was shown in this way for convenience, but they have in fact multi-ramified structure) above was obtained. Number-average molecular weight and weight-average molecular weight of PA-39 obtained through the gel permeation chromatography were 1.51×10^4 and 1.02×10^5 , respectively.

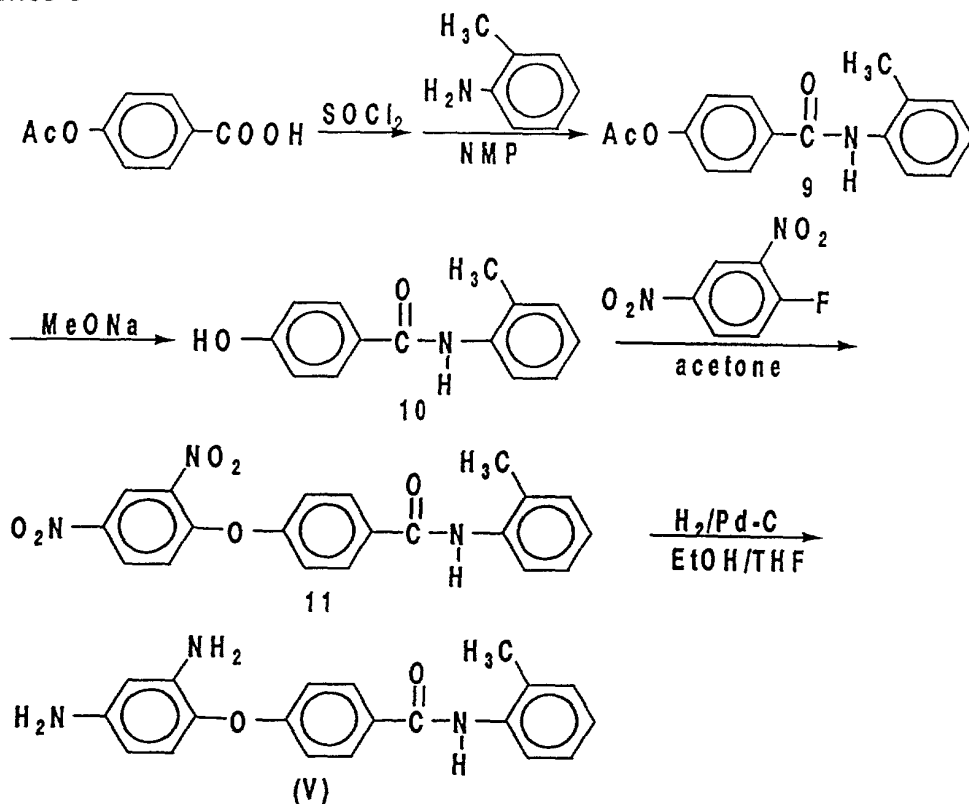
Example 40



Under argon gas atmosphere, 2.95 g (10.0 mmol) of 4,4'-di (chlorocarbonyl) diphenylether and 1.98 g (10.0 mmol) of 4,4'-diaminodiphenyl methane were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to melt and stirred for 4 hours at room temperature. Reaction liquid solution thus obtained was diluted with 37 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 4.68 g of polyamide shown in the structural formula PA-41 above was obtained. Number-

average molecular weight and weight-average molecular weight of PA-41 obtained through the gel permeation chromatography were 1.62×10^4 and 3.77×10^4 , respectively.

Reference 6



3.000 g (16.65 mmol) of 4-acetoxybenzoic acid and 5 ml of thionyl chloride were mixed together and stirred for two hours at 50°C after the addition of a drop of DMF. After thionyl chloride was removed by distillation under the reduced pressure, 5 ml of NMP was added in an ice bath. After stirring for 10 minutes in the ice bath after the addition of 1.784 g (16.65 mmol) of 2-aminotoluene, then the solution was poured into 400 ml of iced water. Precipitate formed was thoroughly washed to yield 3.634 g of 4-acetoxy-2'-methylbenzanilide shown in the structural formula 9 above in colorless solid (Yield : 81.04%).

IR (KBr, cm^{-1}) : 3285, 1759, 1649 (s), 1603 (w), 1586 (w), 1524, 1505, 1456, 1370 (w), 1314, 1202 (s), 1169, 1019 (w), 914 (w), 750 (w), 685 (w).

$^1\text{H-NMR}$ δ (250 MHz, CDCl_3 , ppm) : 2.36 (3H, s), 2.37 (3H, s), 7.15 (1H, m), 7.2-7.3 (4H, m), 7.63 (1H, bs), 7.93-7.96 (3H, m).

3.625 g (13.46 mmol) of 4-acetoxy-2'-methylbenzanilide obtained in the reaction above was dissolved into the solvent mixture with 30 ml of acetone and 10 ml of methanol and cooled to 0°C. 15 ml of sodium methoxide (1 mol/l) was dropwise added into this solution. The solution was made weakly acidic by the addition of 1N hydrochloric acid and then solvent was removed by distillation. Precipitate was thoroughly washed with water and dried to yield 1.592 g of 4-hydroxy-2'-methylbenzanilide shown in the structural formula 10 above in colorless solid (Yield : 52.04 %).

IR (KBr, cm^{-1}) : 3264 (bs), 1620 (s), 1599 (s), 1576, 1537, 1505, 1441, 1377 (w), 1312, 1273 (s), 1229, 1173, 1111 (w), 847 (w), 750, 588 (w).

$^1\text{H-NMR}$ δ (250 MHz, CDCl_3 , ppm) : 2.35 (3H, s), 6.96 (2H, d, $J=8.8\text{Hz}$), 7.1-7.3 (3H, m), 7.6 (1H, d), 7.95 (2H, d, $J=8.8\text{Hz}$), 8.83 (1H, bs), 8.95 (1H, s).

0.990 g (4.356 mmol) of 4-hydroxy-2'-methylbenzanilide and 0.811 g (4.358 mmol) of 2,4-dinitrofluorobenzene were dissolved into 20 ml of acetone. The solution was stirred for one hour at reflux temperature after the addition of 0.6 g (4.3 mmol) of potassium carbonate. The reaction solution was filtered and precipitate was thoroughly washed with acetone. Filtrate was concentrated and purified through column chromatography (developing solvent : chloroform) to yield 1.553 g of 4-(2,4-dinitrophenoxy)-2'-methylbenzanilide shown in the structural formula 11 above in light yellow solid (Yield : 90.63 %).

IR (KBr, cm^{-1}) : 3281 (w), 3086 (s), 1649 (s), 1603, 1526 (s), 1458 (w), 1372, 1356, 1318 (w), 1281, 1198 (w), 909 (w), 866 (w), 837 (w), 743 (w), 503 (w).

$^1\text{H-NMR}$ δ (250 MHz, Acetone- d_6 , ppm) : 2.37 (3H, s), 7.13-7.32 (3H, m), 7.4-7.5 (3H, m), 7.60 (1H, d, $J=7.5\text{Hz}$), 8.22 (2H, d, $J=8.8\text{Hz}$), 8.58 (1H, dd, $J=2.8, 9.0\text{Hz}$), 8.94 (1H, d, $J=2.8\text{Hz}$), 9.16 (1H, bs).

1.55 g (3.90 mmol) of 4-(2,4-dinitrophenoxy)-2'-methylbenzanilide was dissolved into the solvent mixture with 70 ml THF and 30 ml of ethanol, and 0.166 g of 5% Pd-carbon powder was added into this solution. The solution was thoroughly deaerated under the reduced pressure at -78°C , and then stirred for 15 hours after the system was replaced with hydrogen gas and temperature was brought back to room temperature. The solution was concentrated after removing catalyst with Celite to yield 1.26 g of 4-(2,4-diaminophenoxy)-2'-methylbenzanilide shown in the structural formula (V) above in light brown solid (Yield : 96.7 %).

IR (KBr, cm^{-1}) : 3349 (br), 2955 (w), 1626 (s), 1605 (s), 1499 (s), 1456, 1314 (w), 1231 (s), 1167, 851, 754, 596 (w).

$^1\text{H-NMR}$ δ (250 MHz, CDCl_3 , ppm) : 2.14 (3H, s), 4.52 (2H, bs), 4.68 (2H, bs), 5.78 (1H, dd, $J=2.5, 8.4\text{Hz}$), 5.99 (1H, d, $J=2.5\text{Hz}$), 6.50 (1H, d, $J=8.4\text{Hz}$), 6.84 (2H, d, $J=8.8\text{Hz}$), 7.05-7.26 (4H, m), 7.86 (2H, d, $J=8.8\text{Hz}$), 9.64 (1H, s).

EI-MS (m/z) : 333 (M^+), 227 ($\text{M} - \text{toluylamino}$) $^+$, 199 ($\text{M} - \text{CONHC}_7\text{H}_7$) $^+$, 123 (2,4-diaminophenoxyl) $^+$, 106 (toluylanilino) $^+$.

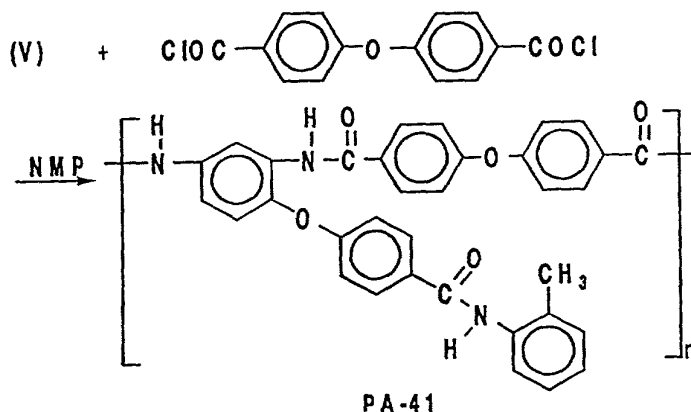
Result of elementary analysis : (Molecular formula: $\text{C}_{20}\text{H}_{19}\text{N}_3\text{O}_2$,

Molecular weight: 333.39)

Calculated value (%) ; C:72.05, H: 5.74, N: 12.60.

Observed value (%) : C:71.78, H:6.14, N:11.62.

Example 41



Under argon gas atmosphere, 1.48 g (5.0 mmol) of 4,4'-di (chlorocarbonyl) diphenylether and 1.67 g (5.0 mmol) of 4-(2,4-diaminophenox)-2'-methylbenzanilide obtained in Reference 6 shown in the formula (V) above were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to room temperature to melt and stirred for one hour at room temperature. Reaction liquid solution thus obtained was diluted with 24 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 2.84 g of polyamide shown in the structural formula PA-41 above was obtained. Number-average molecular weight and weight-average molecular weight of PA-41 obtained through the gel permeation chromatography were 1.02×10^4 and 1.92×10^4 , respectively.

Example 42

Under argon gas atmosphere, 36.3 mg (0.91 mmol) of sodium hydroxide (oil, 60%) was dispersed in 12 ml of DMSO and light yellow homogenous solution was obtained after stirring for one hour at 70°C . The solution was cooled to room

temperature and 0.60 g of polyamide PA-1 obtained in Example 1 was dissolved into the solution and stirred for additional 4 hours. 0.52 g (3.33 mmol) of iodoethane was then added at room temperature and stirred for additional two hours, and precipitate obtained after the solution was poured into excess methanol, filtered and dried to yield 0.57 g of polymer. ¹H-NMR spectrum of polymer obtained was taken and revealed that the product was polyamide (called PA-42 hereafter) in which 27 mole % of amide radical at N position of the structure shown in PA-1 was substituted with ethyl group. Number-average molecular weight and weight-average molecular weight of PA-42 obtained through the gel permeation chromatography were 1.36×10^4 and 2.66×10^4 , respectively.

Example 43

Under argon gas atmosphere, 48.4 mg (1.21 mmol) of sodium hydroxide (oil, 60%) was dispersed in 10 ml of DMSO and light yellow homogenous solution was obtained after stirring for one hour at 70°C. The solution was cooled to room temperature and 0.50 g of polyamide PA-1 obtained in Example 1 was dissolved into the solution and stirred for additional 4 hours, and then 0.57 g (3.35 mmol) of 2-iodopropane was added at room temperature and stirred for additional four hours at 50°C, and precipitate obtained after the solution was poured into excess methanol, filtered and dried to yield 0.53 g of polymer. ¹H-NMR spectrum of polymer obtained was taken and revealed that the product was polyamide (called PA-43 hereafter) in which 7.8 mole % of amide radical at N position of the structure shown in PA-1 was substituted with isopropyl group. Number-average molecular weight and weight-average molecular weight of PA-43 obtained through the gel permeation chromatography were 1.45×10^4 and 3.04×10^4 , respectively.

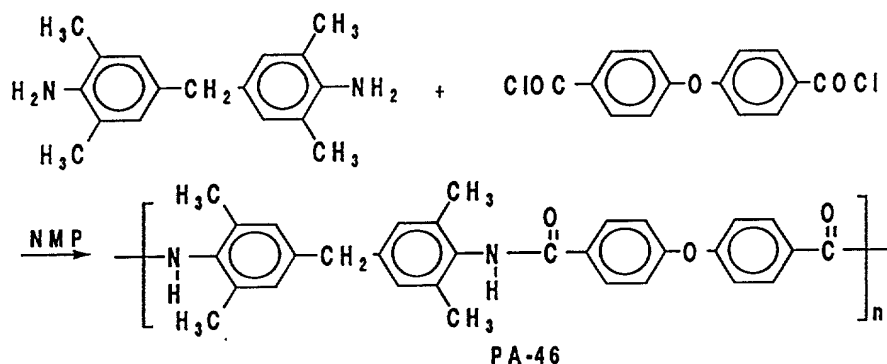
Example 44

Under argon gas atmosphere, 36.3 mg (0.91 mmol) of sodium hydroxide (oil, 60%) was dispersed in 12 ml of DMSO and light yellow homogenous solution was obtained after stirring for one hour at 70°C. The solution was cooled to room temperature and then 0.60 g of polyamide PA-1 obtained in Example 1 was dissolved into the solution and stirred for additional 4 hours. 0.44 g (3.63 mmol) of allylbromide was then added and stirred for additional two hours at room temperature, and precipitate obtained after the solution was poured into excess methanol, filtered and dried to yield 0.58 g of polymer. ¹H-NMR spectrum of polymer obtained was taken and revealed that the product was polyamide (called PA-44 hereafter) in which 23 mole % of amide radical at N position of the structure shown in PA-1 was substituted with allyl group. Number-average molecular weight and weight-average molecular weight of PA-44 obtained through the gel permeation chromatography were 1.66×10^4 and 3.40×10^4 , respectively.

Example 45

Under argon gas atmosphere, 36.3 mg (0.91 mmol) of sodium hydroxide (oil, 60%) was dispersed in 12 ml of DMSO and light yellow homogenous solution was obtained after stirring for one hour at 70°C. The solution was cooled to room temperature and then 0.60 g of polyamide PA-1 obtained in Example was dissolved into the solution and stirred for additional 4 hours. 0.62 g (3.63 mmol) of benzyl bromide was then added and stirred for additional two hours at room temperature, and precipitate obtained after the solution was poured into excess methanol, filtered and dried to yield 0.64 g of polymer. ¹H-NMR spectrum of polymer obtained was taken and revealed that the product was polyamide (called PA-45 hereafter) in which 23 mole % of amide radical at N position of the structure shown in PA-1 was substituted with benzyl group. Number-average molecular weight and weight-average molecular weight of PA-45 obtained through the gel permeation chromatography were 1.60×10^4 and 3.26×10^4 , respectively.

Example 46

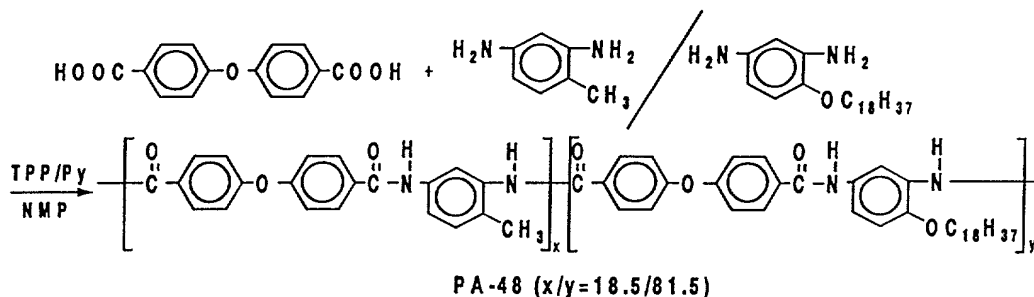


Under argon gas atmosphere, 1.48 g (5.0 mmol) of 4,4'-di (chlorocarbonyl) diphenylether and 1.57 g (5.0 mmol) of 3,3',5,5'-tetramethyl-4,4'-diaminodiphenylmethane were each dissolved to the concentration of 1.0 mol/l in NMP, and mixed at -78°C and frozen. The liquid solution was then gradually heated to melt and stirred for 4 hours at room temperature. Reaction liquid solution thus obtained were diluted with 38 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures described above were repeated and purified, and 2.68 g of polyamide shown in the structural formula PA-46 was obtained. Number-average molecular weight and weight-average molecular weight of PA-46 obtained through the gel permeation chromatography were 1.43×10^4 and 2.49×10^4 , respectively.

Example 47

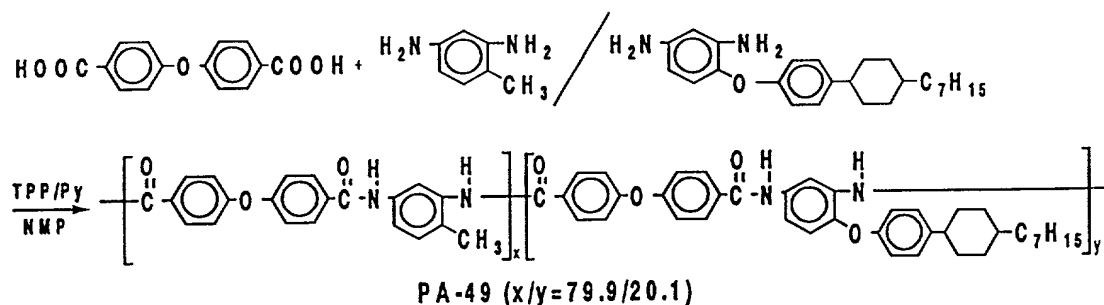
Under argon gas atmosphere, 36.3 mg (0.91 mmol) of sodium hydroxide (oil, 60%) was dispersed in 12 ml of DMSO and light yellow homogenous solution was obtained after stirring for one hour at 70°C. The solution was cooled to room temperature and then 0.60 g of polyamide PA-1 obtained in Example 1 was dissolved into the solution and stirred for additional 4 hours. 1.28 g (3.63 mmol) of 1-iodohexadecane was then added and stirred for additional 4 hours at room temperature, and precipitate obtained after the solution was poured into excess methanol/hexane solvent mixture, filtered and dried to yield 0.59 g of polymer. ¹H-NMR spectrum of polymer obtained was taken and revealed that the product was polyamide (called PA-47 hereafter) in which 19 mole % of amide radical at N position of the structure shown in PA-1 was substituted with hexadecyl group. Number-average molecular weight and weight-average molecular weight of PA-47 obtained through the gel permeation chromatography were 1.59×10^4 and 3.36×10^4 , respectively.

Example 48



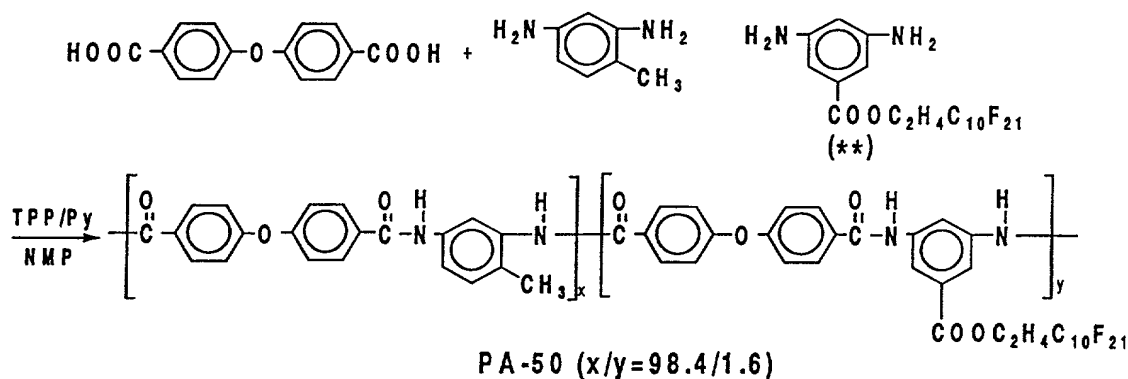
Under argon gas atmosphere, 1.37 g (5.31 mmol) of 4,4'-dicarboxydiphenylether and 0.40 g (1.06 mmol) of 1-octadodecyloxy-2,4-diaminobenzene as well as 0.52 g (4.25 mmol) of 4-methyl-m-phenylenediamine were dissolved in 6.00 ml of NMP, and 1.30 ml of Py and 4.20 ml of TPP were added into this liquid solution and stirred for 17 hours after heated to 100°C. Obtained reaction liquid solution was diluted with 10 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 2.04 g of polyamide shown in the structural formula PA-48 was obtained. ¹H-NMR spectrum of PA-48 was taken and revealed that x/y copolymerization ratio was 81.5/18.5. Number-average molecular weight and weight-average molecular weight of PA-45 obtained through the gel permeation chromatography were 9.30×10^3 and 2.02×10^4 , respectively.

Example 49



Under argon gas atmosphere, 1.36 g (5.26 mmol) of 4,4'-dicarboxydiphenylether and 0.40 g (1.05 mmol) of 4-(4-trans-n-heptylcyclohexylphenoxy)-1,3-diaminobenzene as well as 0.51 g (4.20 mmol) of 4-methyl-m-phenylenediamine were dissolved in 6.00 ml of NMP, and 1.30 ml of Py and 4.20 ml of TPP were added into this liquid solution and stirred for 17 hours after heated to 100°C. Obtained reaction liquid solution was diluted with 10 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified to yield 2.05 g of polyamide shown in the structural formula PA-49. ¹H-NMR spectrum of PA-49 was taken and revealed that x/y copolymerization ratio was 79.9/20.1. Number-average molecular weight and weight-average molecular weight of PA-49 obtained through the gel permeation chromatography were 7.19 x 10³ and 1.47 x 10⁴, respectively.

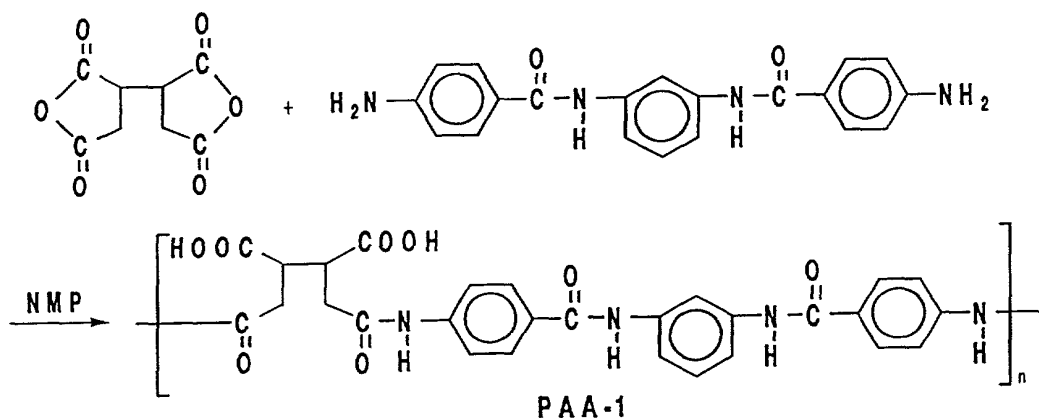
Example 50



Under argon gas atmosphere, 0.30 g (1.16 mmol) of 4,4'-dicarboxydiphenylether and 0.14 g (1.14 mmol) of 4-methyl-m-phenylenediamine

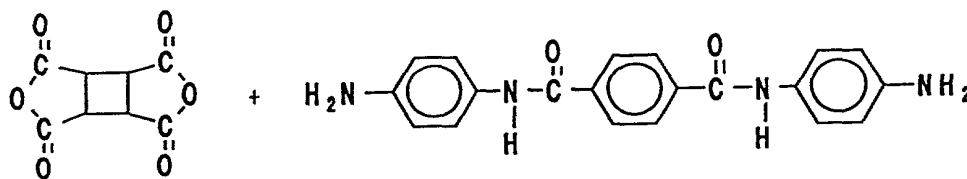
as well as 0.012 g (0.02 mmol) of diamine compound above (**) were dissolved in 1.20 ml of NMP, and 0.30 ml of Py and 0.90 ml of TPP were added into this liquid solution and stirred for 6 hours after heated to 100°C. Obtained reaction liquid solution was diluted with 3 ml of NMP and then poured into excess methanol, and precipitated polymer were filtered and dried. The procedures above were repeated and purified to yield 0.38 g of polyamide shown in the structural formula PA-50. ¹H-NMR spectrum of PA-50 was taken and revealed that x/y copolymerization ratio was 98.4/1.6. Number-average molecular weight and weight-average molecular weight of PA-50 obtained through gel permeation chromatography were 8.49×10^3 and 1.58×10^4 , respectively.

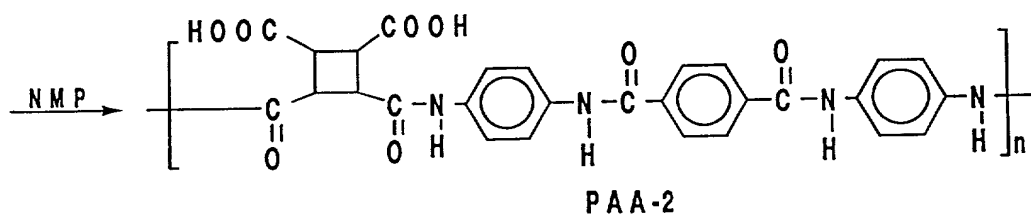
Example 51



Under flowing nitrogen gas, 1.04 g (3.0 mmol) of 1,3-di [4-aminobenzamido] benzene and 0.59 g (3.0 mmol) of 1,2,3,4-butanetetracarboxylic acid di-anhydride were reacted in 9.13 ml of NMP for three hours at room temperature to prepare PAA-1 of polyamide acid shown in the structural formula above. Number-average molecular weight and weight-average molecular weight of PAA-1 obtained through the gel permeation chromatography were 3.35×10^3 and 5.21×10^3 , respectively.

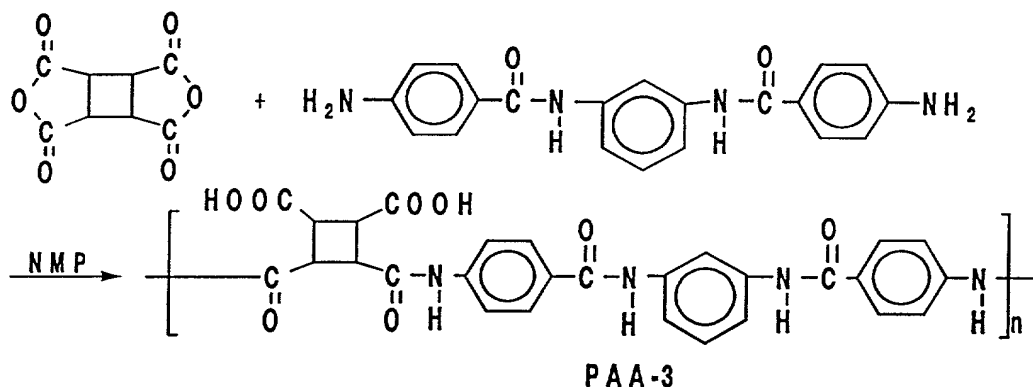
Example 52





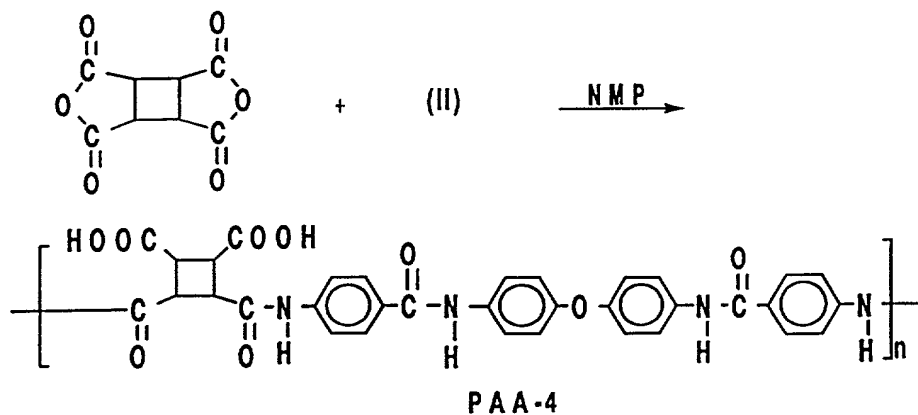
Under flowing nitrogen gas, 3.46 g (10 mmol) of 1,4-di [(4-aminophenyl) carbamoyl] benzene and 1.92 g (9.8 mmol) of 1,2,3,4-cyclobutanetetracarboxylic acid di-anhydride (abbreviated as CBDA hereafter) were reacted in 30.62 ml of NMP for six hours at room temperature to prepare PAA-2 of polyamide acid shown in the structural formula above. Number-average molecular weight and weight-average molecular weight of PAA-2 obtained through the gel permeation chromatography were 7.12×10^3 and 1.65×10^4 , respectively.

Example 53



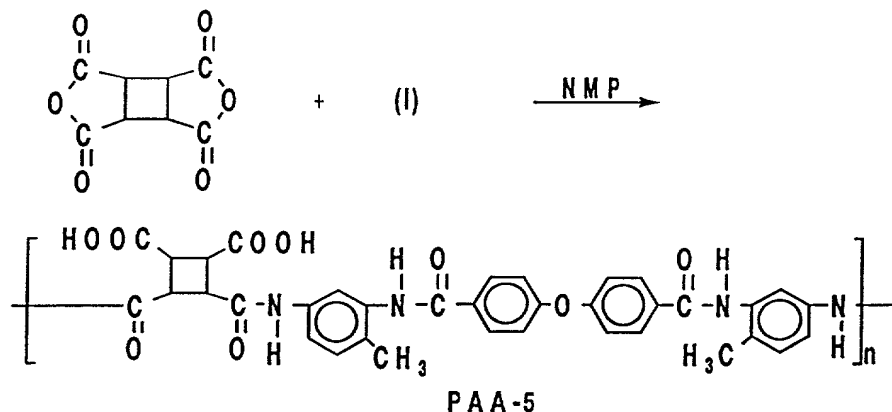
Under flowing nitrogen gas, 1.04 g (3.0 mmol) of 1,3-di [4-aminobenzamide] benzene and 0.58 g (2.94 mmol) of CBDA were reacted in 9.16 ml of NMP for six hours at room temperature to prepare PAA-3 of polyamide acid shown in the structural formula above. Number-average molecular weight and weight-average molecular weight of PAA-3 obtained through the gel permeation chromatography were 3.13×10^4 and 5.45×10^4 , respectively.

Example 54



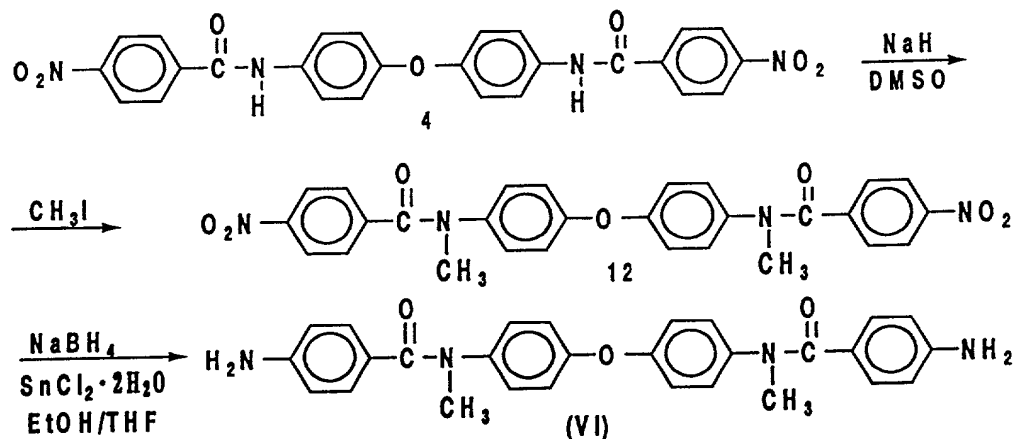
Under flowing nitrogen gas, 1.01 g (2.3 mmol) of 4,4'-di (4-aminobenzamide) diphenylether obtained in Reference 3 shown in the formula (II) and 0.44 g (2.25 mmol) of CBDA were reacted in 8.00 ml of NMP for six hours at room temperature to prepare PAA-4 of polyamide acid shown in the structural formula above. Number-average molecular weight and weight-average molecular weight of PAA-4 obtained through the gel permeation chromatography were 1.50×10^4 and 3.04×10^4 , respectively.

Example 55



Under flowing nitrogen gas, 0.98 g (2.1 mmol) of 4,4'-di [N-(2-methyl-5-aminophenyl) carbonylamino] diphenylether obtained in Reference 2 shown in the formula (I) and 0.40 g (2.06 mmol) of CBDA were reacted in 7.84 ml of NMP for six hours at room temperature to prepare PAA-5 of polyamide acid shown in the structural formula above. Number-average molecular weight and weight-average molecular weight of PAA-5 obtained through the gel permeation chromatography were 6.64×10^4 and 1.08×10^5 , respectively.

Reference 7



Under argon gas atmosphere, 1.64 g (40 mmol) of sodium hydroxide (oil, 60%) was dispersed in 100 ml of DMSO and light yellow homogenous solution after stirring for one hour at 70°C was obtained. The solution was cooled to room temperature and 7.00 g (14.0 mmol) of dinitro compound 4 obtained in Reference 3 was dissolved into the solution and stirred for 4 hours at room temperature. 6.08 g (40 mmol) of iodomethane was then added at room temperature to this solution and the solution was stirred for additional 18 hours, and precipitate was obtained after the solution was poured into 200 ml of water, filtered and dried. 3.56 g of 4,4'-di (N-methyl-4-nitrobenzamide) diphenylether shown in the structural formula 12 above was obtained in light yellow powder after purification through the silica gel chromatography (development solvent : chloroform/ethyl acetate (Yield : 48.3 %).

$^1\text{H-NMR}$ δ (250MHz, CDCl_3 , ppm) : 3.52 (6H, s), 6.82 (4H, d), 7.00 (4H, d), 7.48 (4H, d), 8.08 (4H, d).

2.10 g (3.99 mmol) of 4,4'-di (N-methyl-4-nitrobenzamide) diphenylether was dissolved into the solvent mixture with 50 ml of ethanol and 25 ml of THF and 10.0 g (44.4 mmol) of tin dichloride dihydrate was added. The mixture was heated to 65°C and 378 mg (10 mmol) of sodium boron hydroxide in 50 ml of ethanol was added drop-wise over 4 hours and stirred. The reaction solution was then poured into 300 ml of water and neutralized with 10% sodium hydroxide solution, and precipitate was obtained by filtration. THF was added to this precipitate and soluble matter was extracted by refluxing overnight, and then THF was removed and precipitate was washed with ethanol to yield 1.15 g of 4,4'-di (N-methyl-4-aminobenzamide) diphenylether shown in the structural formula (VI) above in white powder (Yield : 62.0 %).

IR (KBr, cm^{-1}) : 3452, 3333, 3120, 2937, 1363, 1620, 1600.

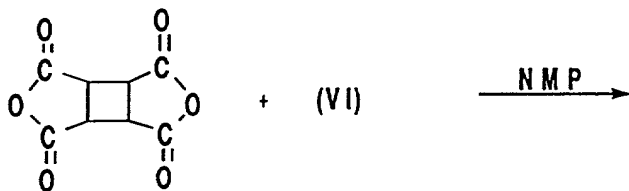
$^1\text{H-NMR}$ δ (250MHz, DMSO-d_6 , ppm) : 3.26 (6H, s), 5.40 (4H, bs), 6.30 (4H, d), 6.80 (4H, d), 6.94 (4H, d), 7.10 (4H, d).

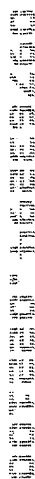
Result of elementary analysis : (Molecular formula: $\text{C}_{28}\text{H}_{26}\text{N}_4\text{O}_3$,
Molecular weight: 466.53)

Calculated value (%) ; C:72.08, H: 5.62, N: 12.00.

Observed value (%) : C:71.60, H:5.65, N:11.76.

Example 56



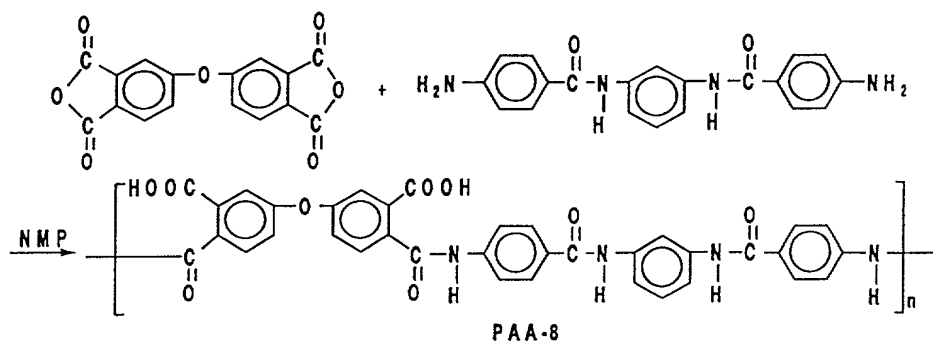


Example 57



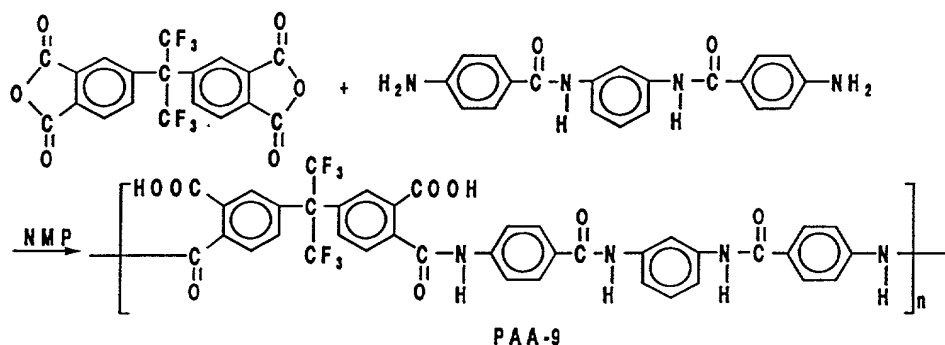
80

Example 58



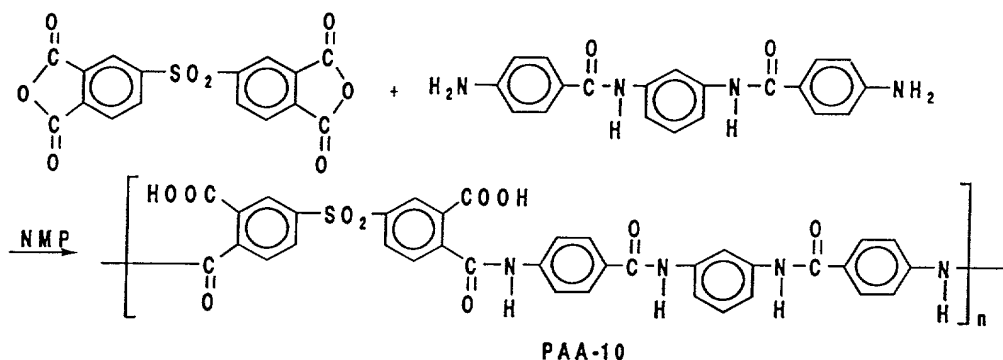
Under flowing nitrogen gas, 1.04 g (3.0 mmol) of 1,3-di [4-aminobenzamide] benzene and 0.93 g (3.0 mmol) of bis (3,4-dicarboxyphenyl) ether dianhydride were reacted in 11.16 ml of NMP for three hours at room temperature to prepare PAA-8 of polyamide acid shown in the structural formula above. Number-average molecular weight and weight-average molecular weight of PAA-8 obtained through the gel permeation chromatography were 1.82×10^4 and 3.33×10^4 , respectively.

Example 59



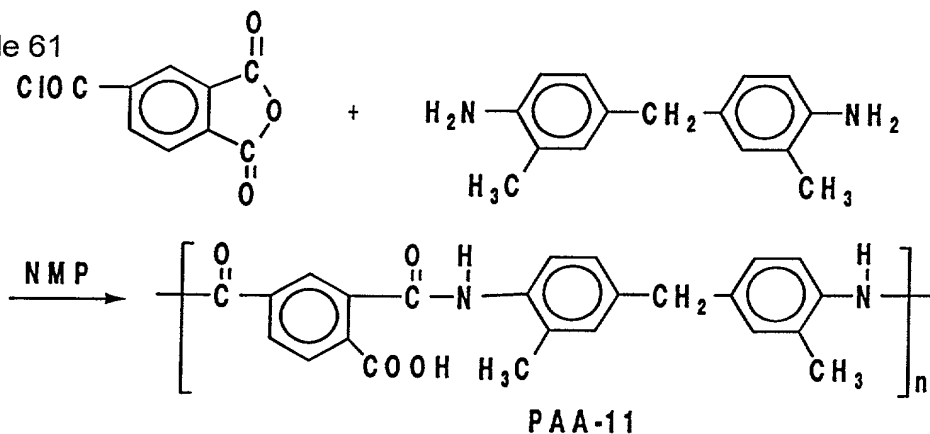
Under flowing nitrogen gas, 1.04 g (3.0 mmol) of 1,3-di [4-aminobenzamide] benzene and 1.33 g (3.0 mmol) of 1,1,1,3,3,3-hexafluoro-2,2-bis (3,4-dicarboxyphenyl) propane dianhydride were reacted in 13.44 ml of NMP for three hours at room temperature to prepare PAA-9 of polyamide acid shown in the structural formula above. Number-average molecular weight and weight-average molecular weight of PAA-9 obtained through the gel permeation chromatography were 2.37×10^4 and 4.22×10^4 , respectively.

Example 60



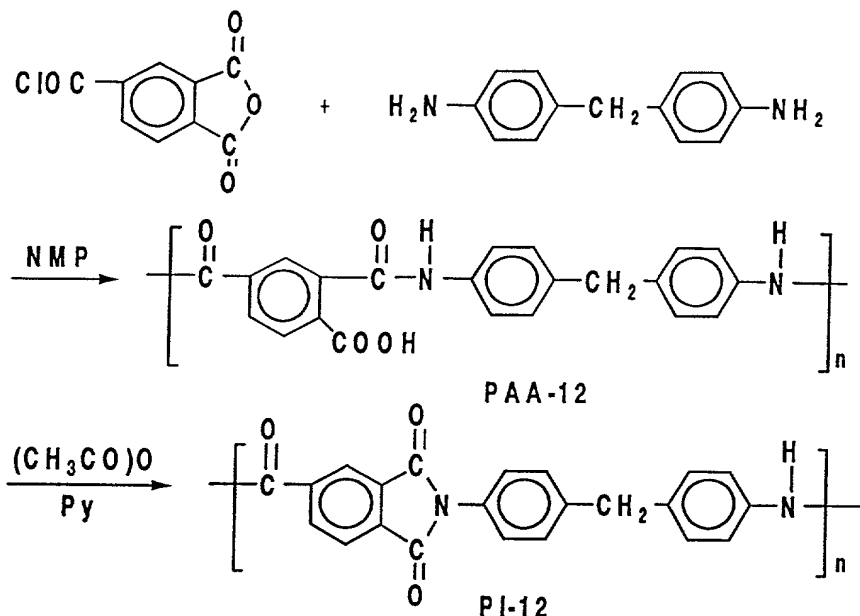
Under flowing nitrogen gas, 1.04 g (3.0 mmol) of 1,3-di [4-aminobenzamide] benzene and 1.07 g (3.0 mmol) of bis (3,4-dicarboxyphenyl) sulfone dianhydride were reacted in 11.98 ml of NMP for three hours at room temperature to prepare PAA-10 of polyamide acid shown in the structural formula above. Number-average molecular weight and weight-average molecular weight of PAA-10 obtained through the gel permeation chromatography were 1.81×10^4 and 3.40×10^4 , respectively.

Example 61



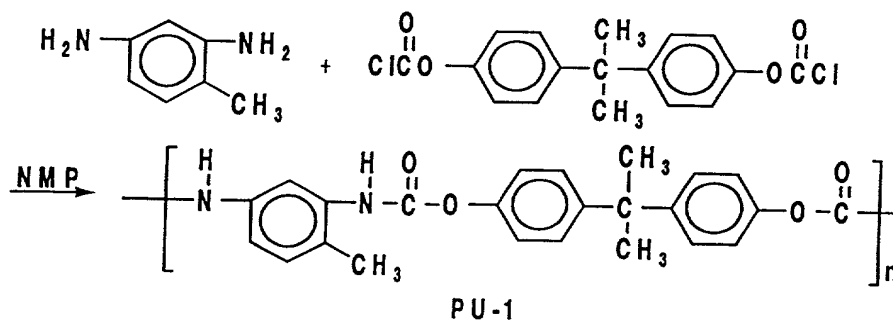
Under argon gas atmosphere, 2.26 g (10 mmol) of 4,4'-diamino-3,3'-dimethyldiphenylmethane and 2.10 g (10 mmol) of trimellitic acid-anhydride acid chloride were dissolved in 24.71 ml of NMP, and stirred for 6 hours after heated to 100°C. Obtained reaction liquid solution was diluted with 45.6 ml of NMP and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 3.88 g of polyamide shown in the structural formula PAA-11 was obtained. Number-average molecular weight and weight-average molecular weight of PA-50 obtained through the gel permeation chromatography were 6.81×10^3 and 1.15×10^4 , respectively.

Example 62



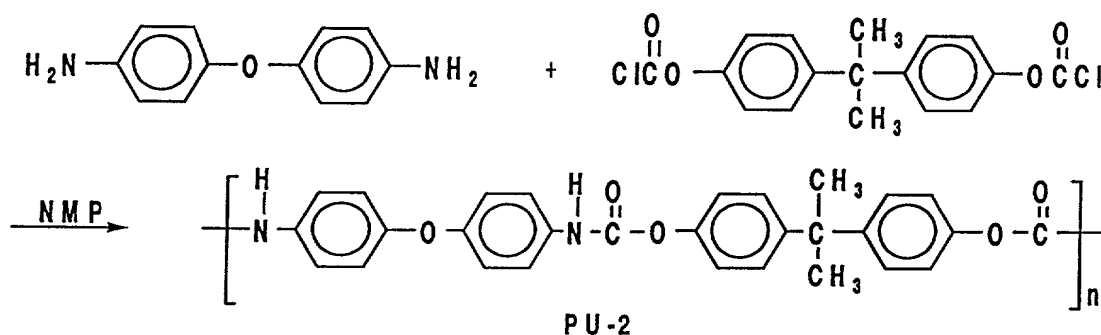
Under argon gas atmosphere, 1.98 g (10 mmol) of 4,4'-diaminodiphenylmethane and 2.10 g (10 mmol) of trimellitic acid-anhydride acid chloride were dissolved in 22.53 ml of NMP, reacted for 6 hours at room temperature to prepare PAA-12 of polyamide acid shown in the structural formula above. Obtained reaction liquid solution was diluted with 7.3 ml of NMP, and 9.50 ml of anhydride acetic acid and 4.90 ml of Py were added and stirred for three hours after heated to 40°C. The reaction solution was then poured into methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 3.26 g of polyimide shown in the structural formula PI-12 above was obtained. Number-average molecular weight and weight-average molecular weight of PI-12 obtained through the gel permeation chromatography were 5.89×10^3 and 1.06×10^4 , respectively.

Example 63



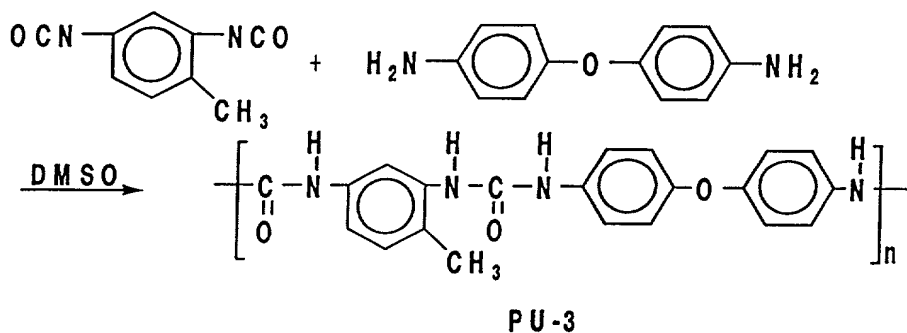
Under argon gas atmosphere, 1.77 g (5.0 mmol) of bisphenol A bis (chloroformate) and 0.61 g (5.0 mmol) of 4-methyl-m-phenylenediamine were dissolved in 13.14 ml of NMP, and stirred for 14 hours at room temperature. Obtained reaction liquid solution was diluted with 18 ml of NMP, and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 1.14 g of polyurethane shown in the structural formula PU-1 above was obtained. Number-average molecular weight and weight-average molecular weight of PU-1 obtained through the gel permeation chromatography were 4.26×10^3 and 5.64×10^3 , respectively.

Example 64



Under argon gas atmosphere, 1.77 g (5.0 mmol) of bisphenol A bis (chloroformate) and 1.00 g (5.0 mmol) of 4,4'-diaminodiphenylether were dissolved in 15.30 ml of NMP, and stirred for two hours between -78°C and room temperature. Obtained reaction liquid solution was diluted with 21 ml of NMP, and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 1.83 g of polyurethane shown in the structural formula PU-2 above was obtained. Number-average molecular weight and weight-average molecular weight of PU-2 obtained through the gel permeation chromatography were 5.63×10^3 and 8.70×10^3 , respectively.

Example 65

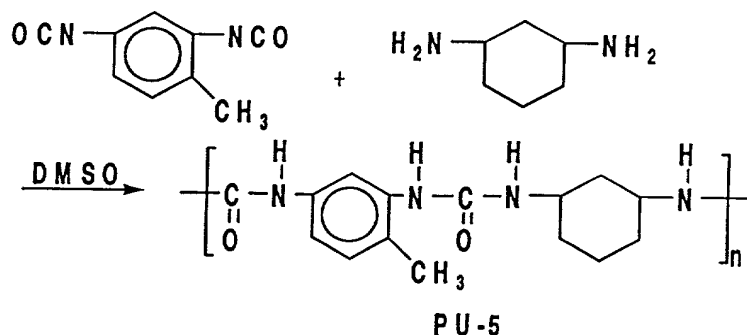


Under argon gas atmosphere, 1.74 g (10.0 mmol) of 4-methyl-1,3-phenylenediisocyanate and 2.00 g (10.0 mmol) of 4,4'-diaminodiphenylether were dissolved in 23.60 ml of DMSO, and stirred for 15 minutes after heated to 60°C. Obtained reaction liquid solution was diluted with 26 ml of DMSO, and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 2.77 g of polyurea shown in the structural formula PU-3 above was obtained. Number-average molecular weight and weight-average molecular weight of PU-3 obtained through the gel permeation chromatography were 1.83×10^4 and 5.40×10^4 , respectively.

Example 66

Under argon gas atmosphere, 85.5 mg (2.14 mmol) of sodium hydroxide (oil, 60%) was dispersed in 20 ml of DMSO and light yellow homogenous solution after stirring for one hour at 70°C was obtained. The solution was cooled to room temperature and 1.0 g (2.67 mmol) of PU-3 of polyurea obtained in Example 65. 0.91 g (6.41 mmol) of iodomethane was then added at room temperature and stirred for another two hours, and precipitate obtained after the solution was poured into excess methanol, filtered and dried to yield 0.93 g of polymer. ¹H-NMR spectrum of polymer was taken and revealed that the product was polyurea (called PU-4 hereafter) in which 19 mole % of urea radical at N position of the structure shown in PU-3 was substituted with methyl group. Number-average molecular weight and weight-average molecular weight of PU-4 obtained through the gel permeation chromatography were 9.79×10^3 and 2.04×10^4 , respectively.

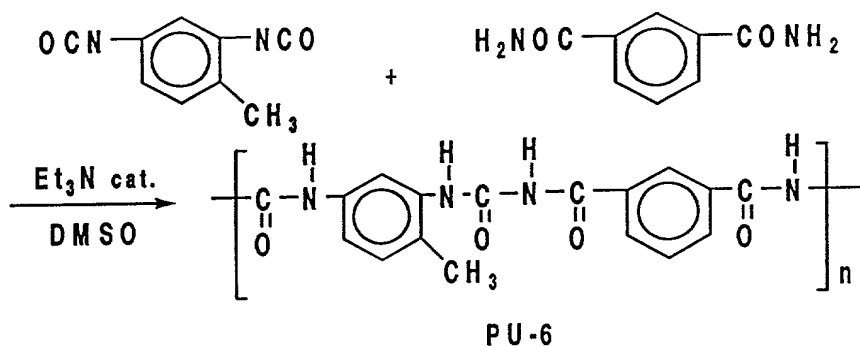
Example 67



Under argon gas atmosphere, 3.05 g (17.5 mmol) of 4-methyl-1,3-

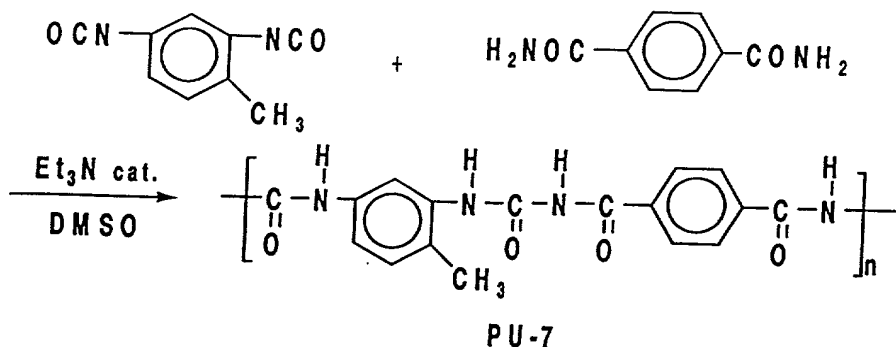
phenylenediisocyanate and 2.00 g (17.5 mmol) of 1,3-diaminocyclohexane were dissolved in 17 ml of DMSO, and stirred for 15 minutes after heated to 60°C. Obtained reaction liquid solution was diluted with 17 ml of DMSO to yield 35 ml of DMSO solution containing 5.05 g of polyurea shown in the structural formula PU-5 above. Number-average molecular weight and weight-average molecular weight of PU-5 obtained through the gel permeation chromatography were 8.91×10^3 and 1.73×10^4 , respectively.

Example 68



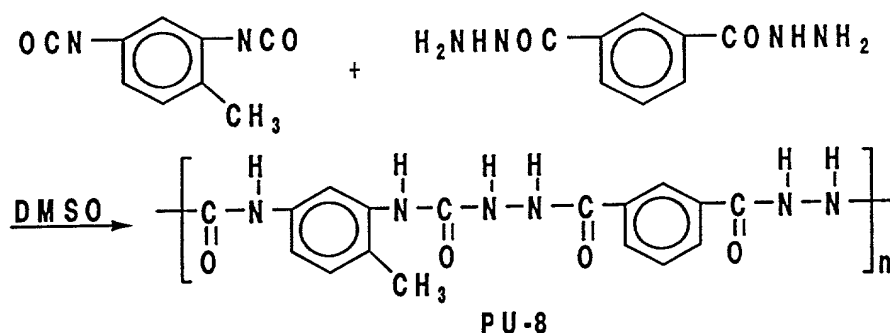
Under argon gas atmosphere, 1.74 g (10.0 mmol) of 4-methyl-1,3-phenylenediisocyanate and 1.64 g (10.0 mmol) of isophthalic acid diazide were dissolved in 15 ml of DMSO and 8.36 ml of triethylamine was also added as a catalyst into the solution, and the solution was stirred for 14 hours after heated to 120°C. Obtained reaction liquid solution was diluted with 24 ml of DMSO, and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 2.67 g of polymer shown in the structural formula PU-6 above was obtained. Number-average molecular weight and weight-average molecular weight of PU-6 obtained through the gel permeation chromatography were 2.41×10^3 and 3.40×10^3 , respectively.

Example 69



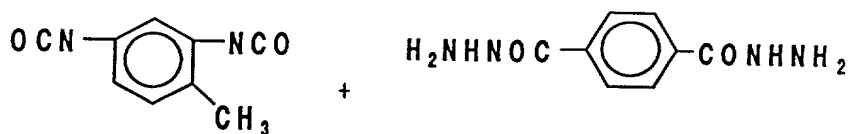
Under argon gas atmosphere, 1.74 g (10.0 mmol) of 4-methyl-1,3-phenylenediisocyanate and 1.64 g (10.0 mmol) of terephthalic acid diazide were dissolved in 15 ml of DMSO and 8.36 ml of triethylamine was also added as a catalyst into the solution, and the solution was stirred for 14 hours after heated to 120°C. Obtained reaction liquid solution was diluted with 24 ml of DMSO, and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 2.54 g of polymer shown in the structural formula PU-7 above was obtained. Number-average molecular weight and weight-average molecular weight of PU-7 obtained through the gel permeation chromatography were 2.39×10^3 and 3.11×10^3 , respectively.

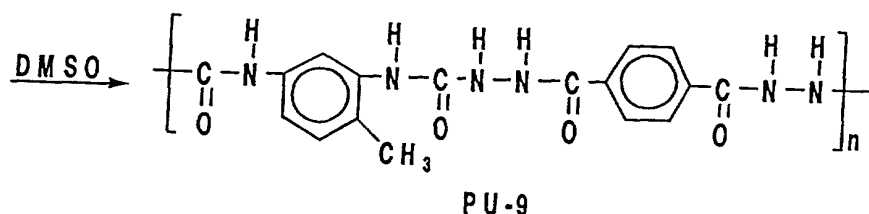
Example 70



Under argon gas atmosphere, 1.74 g (10.0 mmol) of 4-methyl-1,3-phenylenediisocyanate and 1.94 g (10.0 mmol) of isophthalic acid dihydrazide were dissolved in 22.30 ml of DMSO and stirred for 20 minutes after heated to 120°C. Obtained reaction liquid solution was diluted with 26 ml of DMSO, and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 3.50 g of polymer shown in the structural formula PU-8 above was obtained. Number-average molecular weight and weight-average molecular weight of PU-8 obtained through the gel permeation chromatography were 4.54×10^3 and 7.96×10^3 , respectively.

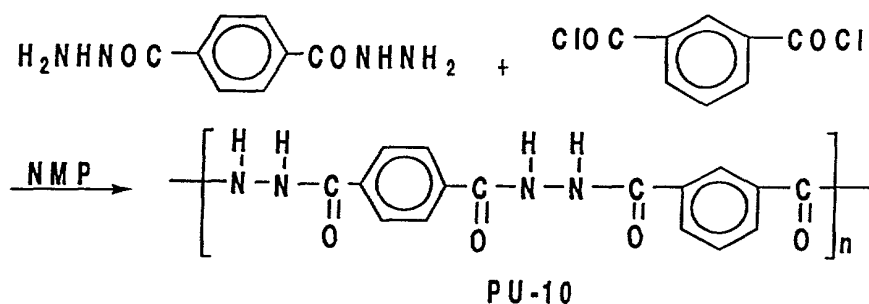
Example 71





Under argon gas atmosphere, 1.74 g (10.0 mmol) of 4-methyl-1,3-phenylenediisocyanate and 1.94 g (10.0 mmol) of terephthalic acid dihydrazide were dissolved in 22.30 ml of DMSO and stirred for 20 minutes after heated to 120°C. Obtained reaction liquid solution was diluted with 26 ml of DMSO, and then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 3.46 g of polymer shown in the structural formula PU-9 above was obtained. Number-average molecular weight and weight-average molecular weight of PU-9 obtained through the gel permeation chromatography were 3.55×10^3 and 6.03×10^3 , respectively.

Example 72



Under argon gas atmosphere, 0.523 g (2.57 mmol) of isophthalic acid dichloride and 0.500 g (2.57 mmol) of terephthalic acid dihydrazide were dissolved in 5.0 ml of MNP and stirred over 4 hours between -78°C and room temperature. The solution was then poured into excess methanol, and polymer precipitated were filtered and dried. The procedures above were repeated and purified, and 0.58 g of polymer shown in the structural formula PU-10 above was obtained. Number-average molecular weight and weight-average molecular weight of PU-10 obtained through the gel permeation chromatography were 5.07×10^3 and 8.15×10^3 , respectively.

Example 73

Under argon gas atmosphere, 168 mg (7.01 mmol) of sodium hydroxide (oil,

1990		1991		1992		1993		1994		1995		1996		1997		1998		1999		2000		2001		2002		2003		2004		2005		2006		2007		2008		2009		2010		2011		2012		2013		2014		2015		2016		2017		2018		2019		2020		2021		2022		2023		2024		2025		2026		2027		2028		2029		2030		2031		2032		2033		2034		2035		2036		2037		2038		2039		2040		2041		2042		2043		2044		2045		2046		2047		2048		2049		2050		2051		2052		2053		2054		2055		2056		2057		2058		2059		2060		2061		2062		2063		2064		2065		2066		2067		2068		2069		2070		2071		2072		2073		2074		2075		2076		2077		2078		2079		2080		2081		2082		2083		2084		2085		2086		2087		2088		2089		2090		2091		2092		2093		2094		2095		2096		2097		2098		2099		2100	
1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100																																																																																																															

PA-1 to PA-50 of polyamide obtained through Example 1 to Example 50 were dissolved into the solvent mixture with NMP and butyl-cellosolve with the desired mixing ratio (ratio by weight), and the solution was adjusted to desired solid concentration thereof. Then, the solution was spincoated with the desired number of rotation over the glass substrate and dried for 5 minutes at 80°C, and heat treated for one hour at 180°C, leading to the uniform polyamide film with 1,000 Å in thickness with any polyamide solution tested. Wavelength with 240 nm – 280 nm or 300 nm - 330 nm of polarized ultraviolet rays from an ultra high-pressure mercury -vapor lamp with 700 W output was time-irradiated over these polyamide polymer films obtained through the band-pass filter (Christiansen filter) and polarizing plate. Liquid crystal cells were prepared with a pair of substrates after they were irradiated with polarized ultraviolet rays under the exactly same condition and with their polyamide film sides facing each other in such a way that the direction of irradiated polarized ultraviolet rays became parallel to each other, and pasted together interposed by 6 μm polymer fine particles. These cells were kept on the hot plate that was maintained beyond the critical anisotropic temperature for liquid crystals and liquid crystals (ZLI-2293 produced by Merck and Co.) were injected. Liquid crystals thus prepared were rotated under the Crossed Nicol of polarizing microscope after they were cooled to room temperature and uniform alignment of the products were confirmed with the observation of clear brightness and darkness without absolutely any shortcomings for any polyamide polymer films tested. The mixing ratio of NMP and BC in each polyamide solution, total solid contents and the number of spincoat rotation for PA-1 to PA-50 are shown in Table 3, and the duration of irradiation with polarized ultraviolet rays when liquid crystal cells were prepared with each polyamide polymer films are shown in Table 4.

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cooled to room temperature. These liquid crystal cells were rotated under the Crossed Nicol of polarizing microscope and the uniform alignment of the products observed before heat-treatment were confirmed to have been maintained with the observation of clear brightness and darkness without absolutely any defects for any cells tested.

Table 3. Mixing ratio of NMP and BC, total solid content and rotation of spincoat for polyamide solution.

Experiment	Polyamide No.	Mixing ratio of NMP and BC	Total solid content (%)	Rotation of spincoat (rpm)
74	PA-1	80 : 20	5.0	4,000
75	PA-2	90 : 10	5.0	3,200
76	PA-3	90 : 10	5.0	3,000
77	PA-4	80 : 20	6.0	3,100
78	PA-5	90 : 10	6.0	2,500
79	PA-6	90 : 10	6.0	2,700
80	PA-7	80 : 20	5.0	2,000
81	PA-8	80 : 20	5.0	2,000
82	PA-9	80 : 20	5.0	2,000
83	PA-10	80 : 20	5.0	2,000
84	PA-11	80 : 20	6.0	3,300
85	PA-12	80 : 20	7.0	2,500
86	PA-13	80 : 20	7.0	2,300
87	PA-14	80 : 20	6.0	2,700
88	PA-15	80 : 20	6.0	2,700
89	PA-16	80 : 20	7.0	3,000
90	PA-17	80 : 20	5.0	2,000
91	PA-18	90 : 10	6.0	2,600
92	PA-19	80 : 20	5.0	2,000
93	PA-20	80 : 20	6.0	2,600
94	PA-21	80 : 20	6.0	3,200
95	PA-22	80 : 20	5.0	2,900
96	PA-23	80 : 20	5.0	3,300
97	PA-24	80 : 20	5.0	3,400
98	PA-25	80 : 20	5.0	3,000
99	PA-26	80 : 20	5.0	4,300
100	PA-27	80 : 20	5.0	2,600

Table 3. Continuation.

Experiment	Polyamide No.	Mixing ratio of NMP and BC	Total solid content (%)	Rotation of spincoat (rpm)
101	PA-28	80 : 20	5.0	3,200
102	PA-29	80 : 20	5.0	3,900
103	PA-30	80 : 20	5.0	2,800
104	PA-31	80 : 20	5.0	2,700
105	PA-32	90 : 10	6.0	3,000
106	PA-33	80 : 20	6.0	3,000
107	PA-34	80 : 20	5.0	3,300
108	PA-35	90 : 10	5.0	2,300
109	PA-36	80 : 20	5.0	3,500
110	PA-37	80 : 20	6.0	2,000
111	PA-38	80 : 20	5.0	3,000
112	PA-39	80 : 20	5.0	2,600
113	PA-40	80 : 20	6.0	3,700
114	PA-41	80 : 20	6.0	2,000
115	PA-42	80 : 20	5.0	3,200
116	PA-43	80 : 20	5.0	3,300
117	PA-44	80 : 20	5.0	3,500
118	PA-45	80 : 20	5.0	3,500
119	PA-46	80 : 20	5.0	3,000
120	PA-47	80 : 20	5.0	3,200
121	PA-48	70 : 30	6.0	2,800
122	PA-49	70 : 30	6.0	3,300
123	PA-50	70 : 30	6.0	2,700

Table 4. Irradiation duration of polarized ultraviolet rays for the preparation of liquid crystal cells with each polyamide polymer film.

Experiment	Polyamide No.	Irradiation duration of polarized ultraviolet rays (sec.)	
		Wavelength (240-280 nm)	Wavelength (300-330 nm)
74	PA-1	720	27
75	PA-2	720	27
76	PA-3	720	27
77	PA-4	720	27
78	PA-5	3600	90
79	PA-6	720	27
80	PA-7	3600	90
81	PA-8	-	450
82	PA-9	720	450
83	PA-10	540	45

Table 4. Continuation.

Experiment	Polyamide No.	Irradiation duration of polarized ultraviolet rays (sec.)	
		Wavelength (240-280 nm)	Wavelength (300-330 nm)
84	PA-11	360	45
85	PA-12	-	90
86	PA-13	-	450
87	PA-14	-	45
88	PA-15	720	45
89	PA-16	720	450
90	PA-17	720	90
91	PA-18	3,600	45
92	PA-19	180	450
93	PA-20	720	90
94	PA-21	720	450
95	PA-22	180	45
96	PA-23	180	14
97	PA-24	360	45
98	PA-25	360	90
99	PA-26	720	23
100	PA-27	54	-
101	PA-28	72	-
102	PA-29	54	-
103	PA-30	54	-
104	PA-31	720	18
105	PA-32	720	23
106	PA-33	720	18
107	PA-34	1,440	180
108	PA-35	1,080	180
109	PA-36	720	90
110	PA-37	1,440	90
111	PA-38	720	180
112	PA-39	720	135
113	PA-40	180	23
114	PA-41	1,440	90
115	PA-42	1,080	45
116	PA-43	720	45
117	PA-44	1,080	45
118	PA-45	1,080	45
119	PA-46	144	-
120	PA-47	3,600	-
121	PA-48	-	90

Table 4. Continuation.

Experiment	Polyamide No.	Irradiation duration of polarized ultraviolet rays (sec.)	
		Wavelength (240-280 nm)	Wavelength (300-330 nm)
122	PA-49	-	450
123	PA-50	720	450

Examples 124-135

Polyamide acid PAA-1 to PAA-11 obtained in Example 51 – Example 61 were dissolved into the mixed solvent with NMP and BC (80 : 20 ratio by weight) and the solution having desired solid concentration of each polyamide acid were prepared. These solution were applied by a spincoat to a glass substrate with desired number of rotation, dried for 5 minutes at 80°C, converted to polyimide PI-1 – PI-11 by the heat treatment for one hour at 250°C, and the uniform polyimide polymer films with 1,000 Å in film thickness were obtained. On the other hand, the uniform polyimide film with 1,000 Å in film thickness was also obtained for PI-12 with the similar method except for heat treatment for one hour at 180°C. Each polyimide polymer films thus obtained were irradiated with 240-280 nm or 300-330 nm of polarized ultraviolet rays for desired time as in Example 74 – Example 123 and the liquid crystal cells were prepared. These liquid crystal cells were rotated under the Crossed Nicol of polarizing microscope and uniform alignment of the products were confirmed with the observation of clear brightness and darkness without absolutely any defects for any polyimide polymer films tested. The total solid contents and the number of spincoat rotation for each polyamide acid PAA-1 to PAA-11 or polyimide solution PI-12 are shown in Table 5, and the duration of irradiation with polarized ultraviolet rays when the liquid crystal cells were prepared with each polyamide polymer films are shown in Table 6.

In addition, the liquid crystal cells of polyimide PI-1 to PI-12 above prepared under each condition were heat-treated for one hour at 120°C in an oven and cooled to room temperature. These liquid crystal cells were rotated under the Crossed Nicol of polarizing microscope and the uniform alignment of the products observed before heat-treatment were confirmed to have been maintained with the observation of clear brightness and darkness without absolutely any defects for any cells tested.

Table 5. Total solid content and the number of spincoat rotation for polyamide acid and polyimide.

Experiment	Polyamide acid and polyimide No.	Total solid content	Number of spincoat rotation
124	PAA-1	7.0	4,500
125	PAA-2	6.0	2,400
126	PAA-3	5.0	4,500
127	PAA-4	5.0	3,100
128	PAA-5	5.0	4,700
129	PAA-6	7.0	3,000
130	PAA-7	5.0	4,000
131	PAA-8	5.0	3,200
132	PAA-9	5.0	4,500
133	PAA-10	6.0	3,800
134	PAA-11	5.0	2,300
135	PAA-12	6.0	2,700

Table 6. Irradiation duration of polarized ultraviolet rays for the preparation of liquid crystal cells with each polyimide polymer film.

Experiment	Polyimide No.	Irradiation duration of polarized ultraviolet rays (sec.)	
		Wavelength (240-289 nm)	Wavelength (300-330 nm)
124	PI-1	720	180
125	PI-2	2,160	270
126	PI-3	360	45
127	PI-4	360	90
128	PI-5	180	90
129	PI-6	360	450
130	PI-7	1,440	270
131	PI-8	720	180
132	PI-9	720	90
133	PI-10	1,440	180
134	PI-11	720	450
135	PI-12	360	450

Examples 136 –146

Polymer PU-1 – PU-11 having similar amide radical of polyurethane and polyurea as obtained in Example 63- to Example 73 were dissolved into the mixed solvent with NMP and BC (80 : 20 ratio by weight) and the solution having desired solid concentration of each component were prepared. These solution were applied by the spincoat to a glass substrate with desired number of rotation, dried

for 5 minutes at 80°C, and heat treated for one hour at 180°C, and the uniform polymer films with 1,000 Å in film thickness were obtained. Each polymer film thus obtained was irradiated with 240-280 nm of polarized ultraviolet rays for desired time as in Example 74 – Example 135 and the liquid crystal cells were prepared. These liquid crystal cells were rotated under the Crossed Nicol of the polarizing microscope and the uniform alignment of the products were confirmed with the observation of clear brightness and darkness without absolutely any shortcomings for any polymer films tested. The total solid contents and the number of spincoat rotation for polymer PU-1 to PU-11 are shown in Table 7, and the duration of irradiation with polarized ultraviolet rays when liquid crystal cells were prepared with each polymer films are shown in Table 8.

Thereafter, the liquid crystal cells of polymer PU-1 to PU-11 above prepared under each condition were heat-treated for one hour at 120°C in an oven and cooled to room temperature. These liquid crystal cells were rotated under the Crossed Nicol of polarizing microscope and the uniform alignment of the products observed before heat-treatment were confirmed to have been maintained with the observation of clear brightness and darkness without absolutely any defects for any cells tested.

Table 7. Total solid content and the number of spincoat rotation for polymer solution having radical similar to amide.

Experiment	Polymer No. having radical similar to amide	Total solid content	Number of spincoat rotation
136	PU-1	6.0	2,700
137	PU-2	6.0	2,200
138	PU-3	5.0	3,200
139	PU-4	6.0	2,800
140	PU-5	7.0	3,300
141	PU-6	7.0	2,000
142	PU-7	7.0	2,000
143	PU-8	6.0	2,300
144	PU-9	6.0	2,000
145	PU-10	6.0	2,000
146	PU-11	7.0	2,800

Table 8. Irradiation duration of polarized ultraviolet rays for the preparation of liquid crystal cells with each polymer having radical similar to amide film.

Experiment	Polymer No. having radical similar to amide	Irradiation duration of polarized ultraviolet rays (sec.)
		Wavelength (240-289 nm)
136	PU-1	180
137	PU-2	3,600
138	PU-3	72
139	PU-4	144
140	PU-5	360
141	PU-6	720
142	PU-7	360
143	PU-8	3,600
144	PU-9	180
145	PU-10	1,440
146	PU-11	1,440

Comparative Example 1.

6•6 nylon (molecular weight ca. 20,000, glass transition temperature 45°C) was dissolved in m-cresol to prepare the solution with a total solid concentration of 4%. The solution was applied on the glass substrate by spincoating at 5,000 rpm, followed by drying for 5 minutes at 120°C and heat treating for one hour at 180°C, the polyamide polymer film with 1,000 Å in thickness were prepared. Polarized ultraviolet rays of wavelength 240 nm – 280 nm for one hour or 300 nm – 330 nm for 15 minutes were irradiated to this 6•6 nylon film just like in Examples and the liquid crystal cells were prepared. These cells were rotated under the Crossed Nicol of polarizing microscope and they did not show any brightness and darkness as well as no alignment of liquid crystal.

Comparative Example 2

1.83 g (10.0 mmol) of adipic acid chloride and 1.08 g (10.0 mmol) of m-phenylenediamine were dissolved in 20.29 ml of NMP, and 1.94 ml of Py was added to this solution and stirred for three hours from –78°C to room temperature. After diluting the obtained solution with 15 ml of NMP, the solution was poured into methanol and polymer precipitated were filtered and dried. The procedures above were repeated and purified to yield 2.18 g of polyamide. Number-average molecular weight and weight-average molecular weight of the polyamide obtained through the gel permeation chromatography were 1.09×10^4 and 2.62×10^4 , respectively.

The polyamide was made into the solution with the total solid concentration of 5% by dissolving in the mixed solvent with NMP and BC (9: 1 ratio by weight). The solution was applied on the glass substrate by spincoating at 3,000 rpm, followed by drying for 5 minutes at 80°C and heat treating for one hour at 180°C, the polyamide polymer film with 1,000 Å in thickness was prepared. Polarized ultraviolet rays of wavelength 240 nm – 280 nm for one hour or 300 nm – 330 nm for 15 minutes were irradiated to this polyamide film just like in Examples and the liquid crystal cells were prepared. These cells were rotated under the Crossed Nicol of polarizing microscope and they did not show any brightness and darkness as well as no alignment of liquid crystal.

Comparative Example 3

Under flowing nitrogen gas, 2.03 g (10.0 mmol) of isophthalic acid chloride and 0.88 g (10.0 mmol) of 1,4-diaminobutane were dissolved in 20.29 ml of NMP, and 1.94 ml of Py was added to this solution and stirred for three hours from –78°C to room temperature. After diluting the obtained solution with 15 ml of NMP, the solution was poured into methanol and polymer precipitated were filtered and dried. The procedures above were repeated and purified to yield 2.07 g of polyamide. Number-average molecular weight and weight-average molecular weight of the polyamide obtained through the gel permeation chromatography were 6.53×10^3 and 1.30×10^3 , respectively.

This polyamide was made into the solution with the total solid concentration of 4% by dissolving in m-cresol. The solution was applied on the glass substrate by spincoating at 5,000 rpm, followed by drying for 5 minutes at 120°C and heat treated for one hour at 180°C, the polyamide polymer film with 1,000 Å in thickness was prepared. Polarized ultraviolet rays of wavelength 240 nm – 280 nm for one hour or 300 nm – 330 nm for 15 minutes were irradiated to this polyamide film just like in Examples and the liquid crystal cells were prepared. These cells were rotated under the Crossed Nicol of polarizing microscope and they did not show any brightness and darkness as well as no alignment of liquid crystal.

Comparative Example 4

Under flowing nitrogen gas, 2.14 g (9.8 mmol) of pyromellitic dianhydride and 2.00 g (10.0 mmol) of 4,4'-diaminodiphenylether were dissolved in 27.60 ml of NMP and reacted for two hours at room temperature to prepare polyimide precursor solution. Polymerization reaction went without difficulty and with uniformity. Number-average molecular weight and weight-average molecular weight of the polyimide precursor obtained through the gel permeation chromatography were 3.45×10^4 and 5.73×10^4 , respectively.

The polyimide precursor was made into the solution with the total solid concentration of 4% by dissolving in the mixed solvent with NMP and BC (4 : 1 ratio by weight). The solution was applied on the glass substrate by spincoating at 4,000 rpm, followed by drying for 5 minutes at 80°C and heat treated for one hour at 250°C, the polyimide polymer film with 1,000 Å in thickness was prepared. Polarized ultraviolet rays of wavelength 240 nm – 280 nm for one hour or 300 nm – 330 nm for 15 minutes were irradiated to this polyimide film just like in Examples and the liquid crystal cells were prepared. These cells were rotated under the Crossed Nicol of polarizing microscope and they did have many defects with some degree of brightness and darkness, and liquid crystal-alignment was not uniform.

Comparative Example 5.

Polyvinyl cinnamate (molecular weight of ca. 20,000) was made into the solution with the total solid concentration of 2 weight % by dissolving in the mixed solvent with monochlorobenzene and dichloromethane. The solution was applied on the glass substrate by spincoating at 2,000 rpm, followed by drying for 5 minutes at 80°C and heat treated for one hour at 100°C, the coat film with 1,000 Å in thickness was prepared. Polarized ultraviolet rays of wavelength 300 nm – 330 nm for 60 seconds were irradiated to this polyvinyl cinnamate film just like in Examples and the liquid crystal cells were prepared. These liquid crystal cells were rotated under the Crossed Nicol of polarizing microscope and the uniform alignment of the products were confirmed with the observation of clear brightness and darkness without absolutely any defect, but these liquid crystal cells after having heat-treated for one hour at 120°C in an oven and cooled to room temperature showed many defects when observed under the Crossed Nicol of polarizing microscope and the alignment observed before heat-treatment have been confirmed to have lost and the alignment was not in order any longer.

Comparative Example 6

Under flowing nitrogen gas, 1.92 g (9.8 mmol) of CBDA and 4.10 g (10.0 mmol) of 2,2-bis [4-(4-aminophenoxy) phenyl] propane were dissolved in 40.13 ml of NMP and reacted for three hours at room temperature to prepare polyimide precursor solution. Polymerization reaction went without difficulty and with uniformity. Number-average molecular weight and weight-average molecular weight of the polyimide precursor obtained through the gel permeation chromatography were 2.74×10^4 and 4.19×10^4 , respectively.

The polyimide precursor was made into the solution with the total solid concentration of 4% by dissolving in the mixed solvent with NMP and BC (4 : 1 ratio by weight). The solution was applied on the glass substrate by spincoating at

4,300 rpm, followed by drying for 5 minutes at 80°C and heat treated for one hour at 250°C, the polyimide polymer film with 1,000 Å in thickness was prepared. Polarized ultraviolet rays of wavelength 240 nm – 280 nm for 12 minutes were irradiated to this polyimide film just like in Examples and the liquid crystal cells were prepared. These liquid crystal cells were rotated under the Crossed Nicol prism of polarizing microscope and the uniform alignment of the products were confirmed with the observation of clear brightness and darkness without absolutely any shortcomings, but these liquid crystal cells after having heat-treated for one hour at 120°C in an oven and cooled to room temperature showed various defects when observed under the Crossed Nicol of polarizing microscope and the alignment observed before heat-treatment have been confirmed to have lost and the alignment was not in order any longer.

Comparative Example 7.

Under flowing nitrogen gas, 1.92 g (9.8 mmol) of CBDA and 2.40 g (10.0 mmol) of diamine compound (III) shown in Example 34 above were dissolved in 23.86 ml of NMP and reacted for 6 hours at room temperature to prepare polyimide precursor solution. Polymerization reaction went without difficulty and with uniformity. Number-average molecular weight and weight-average molecular weight of the polyimide precursor obtained through the gel permeation chromatography were 6.64×10^4 and 1.08×10^5 , respectively.

The polyimide precursor was made into the solution with the total solid concentration of 4% by dissolving in the mixed solvent with NMP and BC (4 : 1 ratio by weight). The solution was applied on the glass substrate by spincoating at 4,300 rpm, followed by drying for 5 minutes at 80°C and heat treated for one hour at 250°C, the polyimide polymer film with 1,000 Å in thickness was prepared. Polarized ultraviolet rays of wavelength 240 nm – 280 nm for one hour or 300 nm – 33- nm for 15 minutes were irradiated to this polyimide film just like in Examples and the liquid crystal cells were prepared. These liquid crystal cells were rotated under the Crossed Nicol of polarizing microscope and some degree of brightness and darkness were observed with various defects and the alignment was not in order at all.

Comparative Example 8

Under flowing nitrogen gas, 1.92 g (9.8 mmol) of CBDA and 3.60 g (10.0 mmol) of diamine compound (IV) shown in Example 38 were dissolved in 24.96 ml of NMP and reacted for 6 hours at room temperature to prepare polyimide precursor solution. Polymerization reaction went without difficulty and with uniformity. Number-average molecular weight and weight-average molecular weight of the polyimide precursor obtained through the gel permeation chromatography were

6.73×10^3 and 1.17×10^4 , respectively.

The polyimide precursor was made into the solution with the total solid concentration of 6% by dissolving in the mixed solvent with NMP and BC (4 : 1 ratio by weight). The solution was applied on the glass substrate by spincoating at 2,400 rpm, followed by drying for 5 minutes at 80°C and heat treated for one hour at 250°C, the polyimide polymer film with 1,000 Å in thickness was prepared. Polarized ultraviolet rays of wavelength 240 nm – 280 nm for one hour or 300 nm – 33 nm for 15 minutes were irradiated to this polyimide film just like in Examples and the liquid crystal cells were prepared. These liquid crystal cells were rotated under the Crossed Nicol of polarizing microscope and some degree of brightness and darkness were observed with many defects and the alignment was not in order at all.

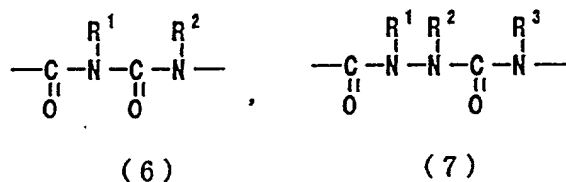
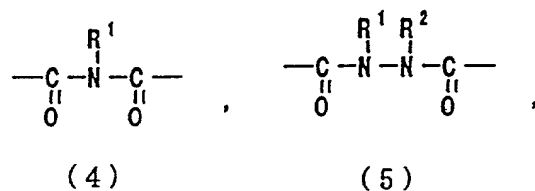
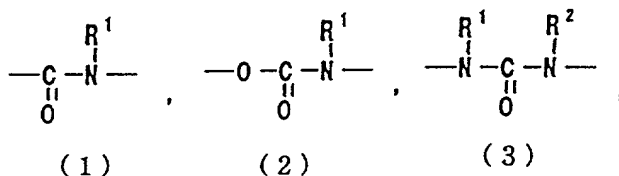
Industrial Applicability

Thin polymer film formed with a liquid crystal-alignment agent in the present invention on the substrate can achieve uniform and stable alignment of liquid crystal molecules by the light or electron rays without rubbing action required in the past. In addition, the alignment thereof achieved high heat stability and high light resistance. Therefore, the practical industrial productivity of liquid crystal elements can be improved with the particular use of the liquid crystal-aligning agent in the present invention.

Claims

Claim 1.

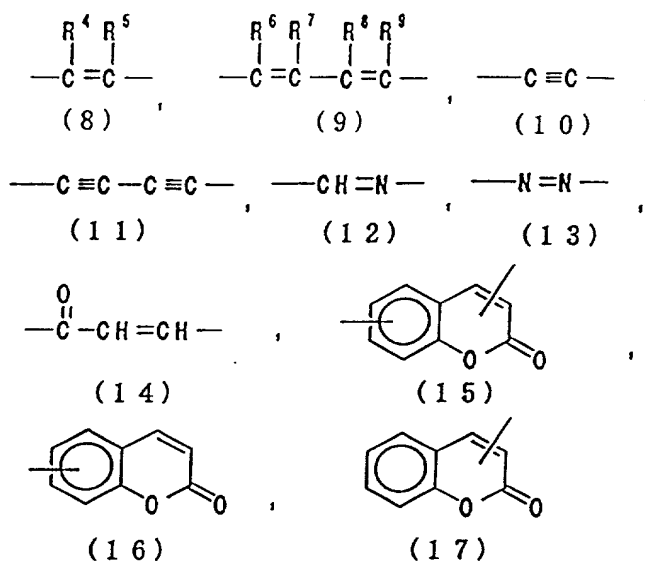
Liquid crystal alignment agent which form the liquid crystal alignment film comprising of a thin alignment film over the substrate where irradiation of light or electron rays align liquid crystal molecules without any rubbing treatment, and said liquid crystal alignment agent comprising of polymer compound having bonds shown in the general formula (1) – (7) below



wherein R¹, R² and R³ are independently of each other hydrogen, alkyl, substituted alkyl, aryl or propargyl; in the main chain of polymer compound with number-average molecular weight of 1,000 – 300,000, and said bond makes the direct bond with either divalent or trivalent aromatic group at the both ends of said bond or with divalent or trivalent aromatic group making the direct bond at one end of said bond while at the other forming the direct bond with divalent or trivalent alicyclic hydrocarbon group.

Claim 2.

Liquid crystal alignment agent according to Claim 1, where the main chain or side chain of the polymer having no functional groups shown in the general formula (8) – (17) below



wherein R^4 , R^5 , R^6 , R^7 , R^8 and R^9 are independently of each other hydrogen, halogen, alkyl, substituted alkyl, substituted alkoxy, carboxyl, alkoxycarbonyl or cyano group as substituent group which may lead to dimerization reaction or isomerization reaction by the irradiation with light or electron rays.

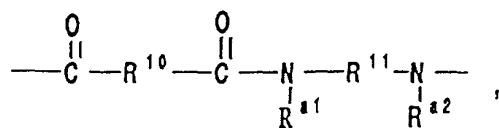
Claim 3.

Liquid crystal alignment agent according to Claim 1 or Claim 2, where said polymer is polyamide.

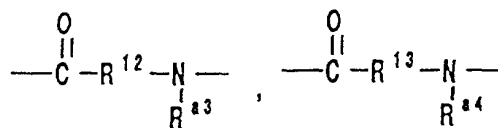
Claim 4.

Liquid crystal alignment agent according to Claim 3, where said polymer compound is polyamide having the repeating unit comprising of the general

formula (18) or of the general formula (19a) and (19b) below



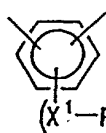
(18)



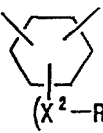
(19a)

(19b)

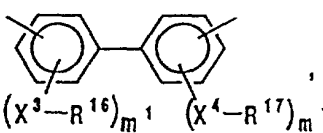
wherein R¹⁰, R¹¹, R¹² and R¹³ are divalent organic radical in the general formula (20) – (23)



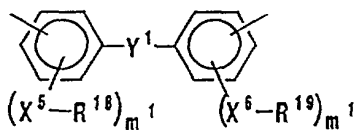
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(21)

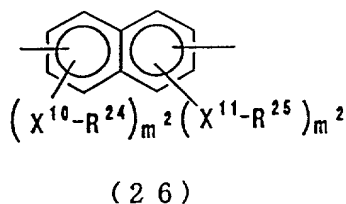
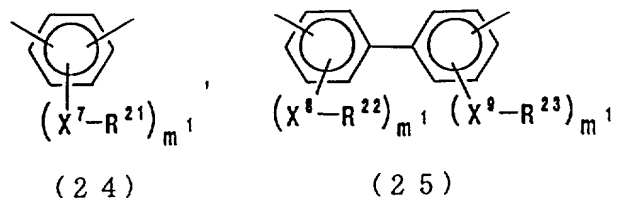


(22)



(23)

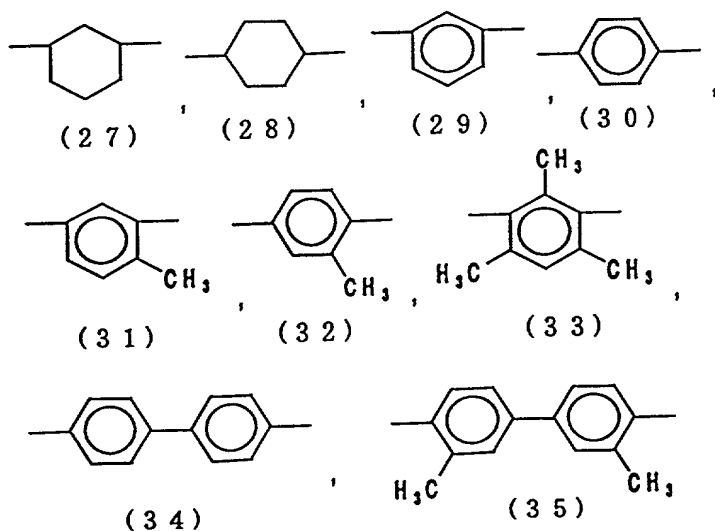
wherein X¹, X², X³, X⁴, X⁵ and X⁶ are independently of each other single bond, O, CO₂, OCO, CH₂O, NHCO or CONH; R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸ and R¹⁹ are independently of each other hydrogen, halogen, C₁-C₂₄ alkyl, C₁-C₂₄ alkyl containing fluorine, aryl, propargyl, phenyl or substituted phenyl; Y¹ is O, S, CO, CO₂, SO₂, CH₂, NH, NHCO, Y²-Ar¹-Y³, Y⁴-(CH₂)_n¹-Y⁵ or Y⁶-Ar²-R²⁰-Ar³-Y⁷; Y², Y³, Y⁴, Y⁵, Y⁶ and Y⁷ are independently of each other O, S, CO, CO₂, SO₂, CH₂, NH or NHCO; n¹ is an integer of 1-10; R²⁰ is C₁-C₅ straight or branched lower alkylene, fluoroalkylene or alkylenedioxy, and further Ar¹, Ar² and Ar³ are independently of each other divalent organic radical in general formula (24), (25) or (26) below

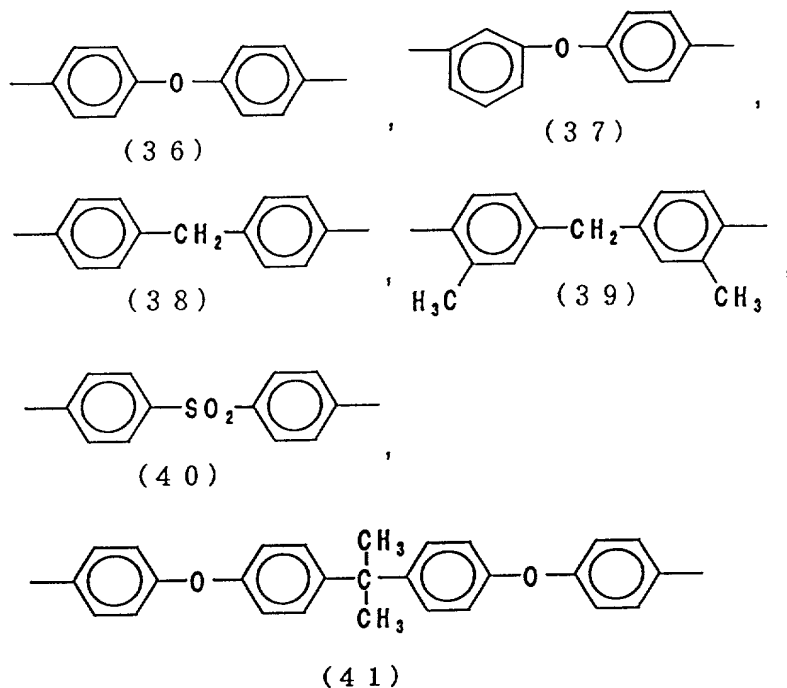


wherein X^7 , X^8 , X^9 , X^{10} and X^{11} are independently of each other single bond, O, CO_2 , OCO , CH_2O , NHCO or CONH ; R^{21} , R^{22} , R^{23} , R^{24} and R^{25} are independently of each other hydrogen, halogen, $\text{C}_1\text{-C}_{24}$ alkyl, $\text{C}_1\text{-C}_{24}$ alkyl containing fluorine, aryl, propargyl, phenyl or substituted phenyl; m^1 is an integer of 1 - 4; m^2 is an integer of 1 - 3, with the proviso that R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{21} , R^{22} , R^{23} , R^{24} and R^{25} are either hydrogen or halogen, then X^1 , X^2 , X^3 , X^4 , X^5 , X^6 , X^7 , X^8 , X^9 , X^{10} and X^{11} are single bond; and R^{a1} , R^{a2} , R^{a3} and R^{a4} are independently of each other hydrogen, alkyl, substituted alkyl, aryl or propargyl.

Claim 5.

Liquid crystal alignment agent according to Claim 3 or Claim 4, where R^{10} or R^{11} in the general formula (18) above or R^{12} and R^{13} in the general formula (19a) and (19b) are independently of each other radical selected from the formula (27) – (41) below



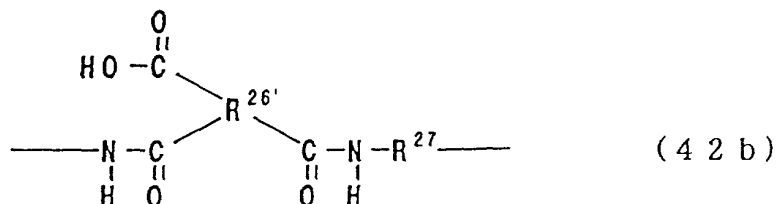
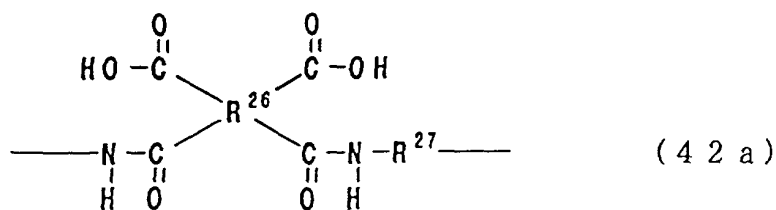


Claim 6.

Liquid crystal alignment agent according to Claim 1 or Claim 2, where said polymer compound is polyimide precursor or polyimide obtained by chemical or heat imidization of said polyimide precursor.

Claim 7.

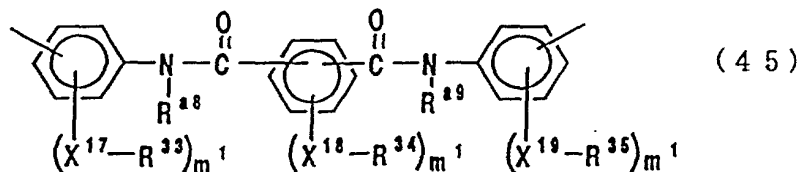
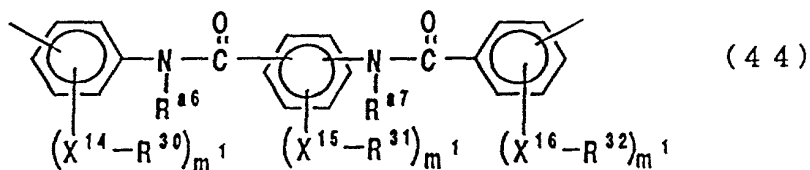
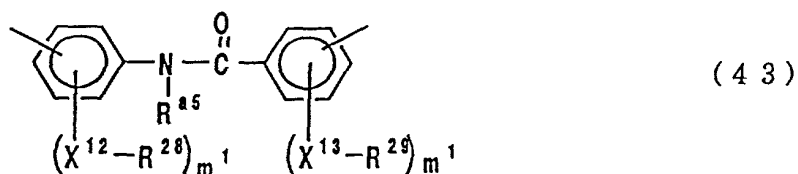
Liquid crystal alignment agent according to Claim 6 where said polymer compound is polyimide precursor or polyimide obtained by chemical or heat imidization of said polyimide precursor with the repeating unit comprising of the general formula (42a) and (42b) below

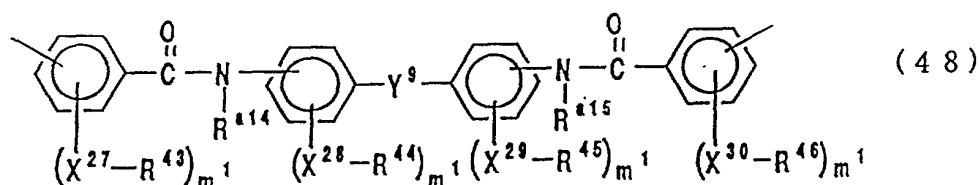
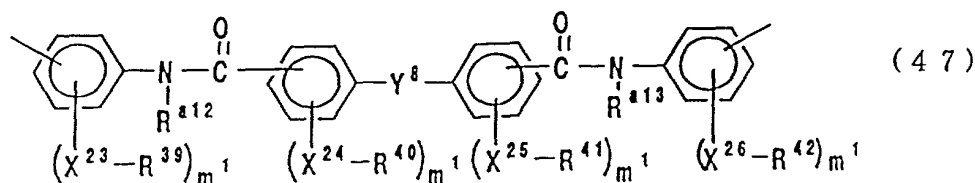
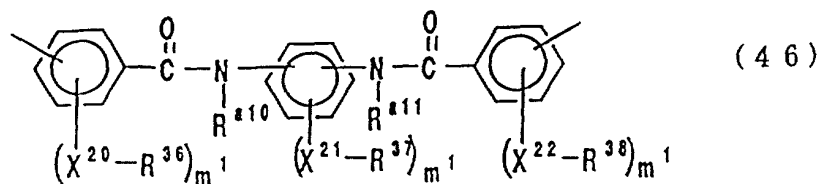


wherein R^{26} is tetravalent organic radical; $\text{R}^{26'}$ is trivalent organic radical; and R^{27} is divalent organic radical containing amide radical bonded with divalent or trivalent aromatic or alicyclic hydrocarbon group.

Claim 8.

Liquid crystal alignment agent according to Claim 6 or Claim 7, where R^{27} in the general formula (42a) and (42b) above is selected from the general formula (43) – (48) below

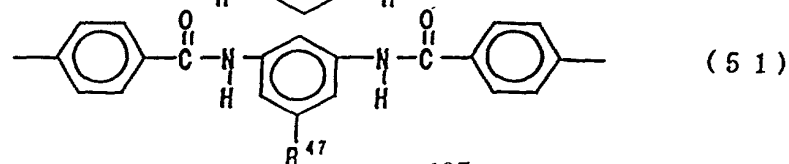
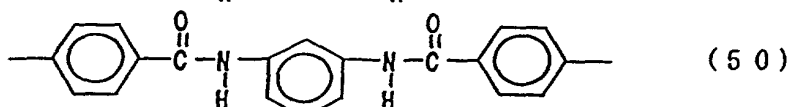
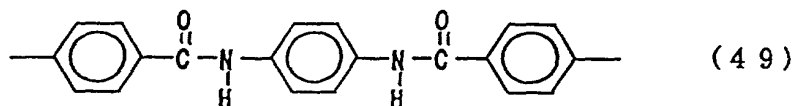


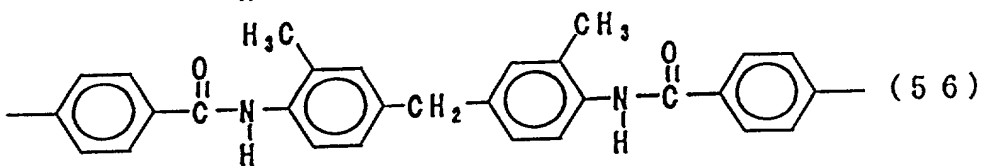
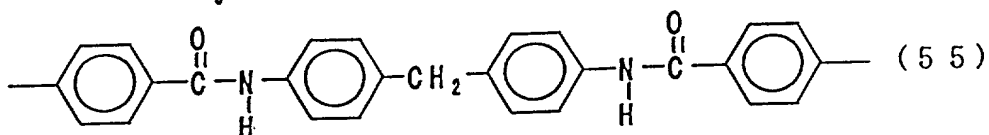
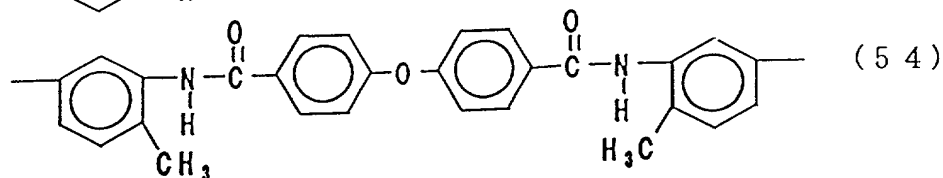
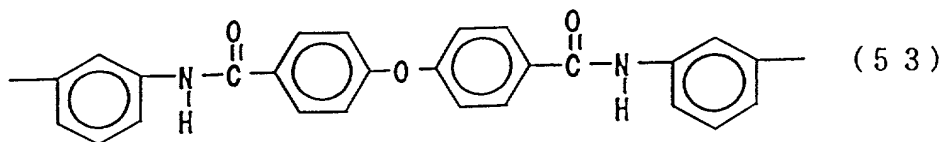
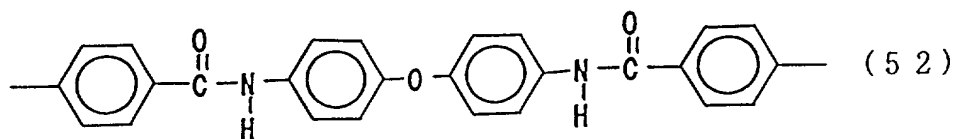


wherein $X^{12} - X^{30}$ are independently of each other single bond, O, CO_2 , OCO or CH_2O ; $R^{28} - R^{46}$ are independently of each other hydrogen, halogen, $\text{C}_1\text{-C}_{24}$ alkyl, $\text{C}_1\text{-C}_{24}$ alkyl containing fluorine, aryl, propargyl, phenyl or substituted phenyl; $R^{a5} - R^{a15}$ are independently of each other hydrogen, alkyl, substituted alkyl, aryl or propargyl; Y^8 and Y^9 are O, S, SO_2 , CH_2 , NH, NHCO or CONH; and m^1 is an integer of 1 - 4 with the proviso that $R^{28} - R^{46}$ are hydrogen or halogen, then $X^{12} - X^{30}$ are single bond.

Claim 9.

Liquid crystal alignment agent according to any one of Claim 6 through Claim 8, where radical for R^{27} in the general formula (42a) and (42b) above is selected from in the formula (49) - (56) below





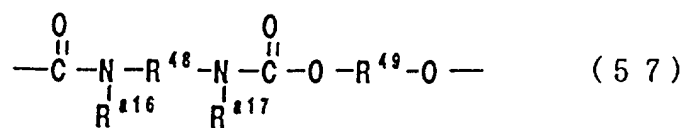
wherein R⁴⁷ is halogen, C₁-C₂₄ alkyl, C₁-C₂₄ alkoxy or C₁-C₂₄ alkoxycarbonyl.

Claim 10.

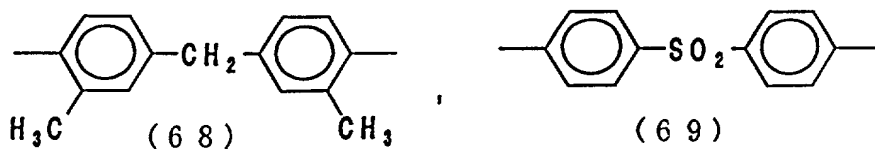
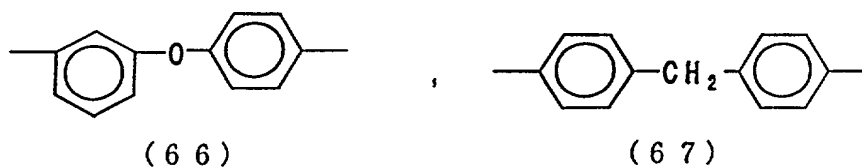
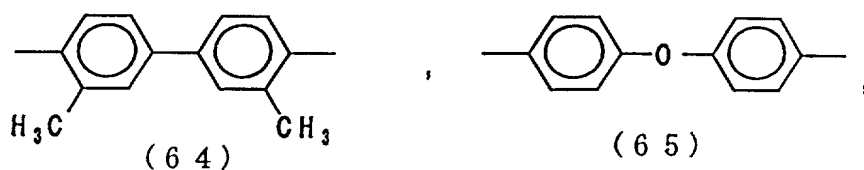
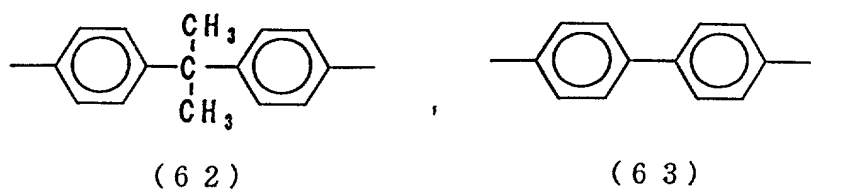
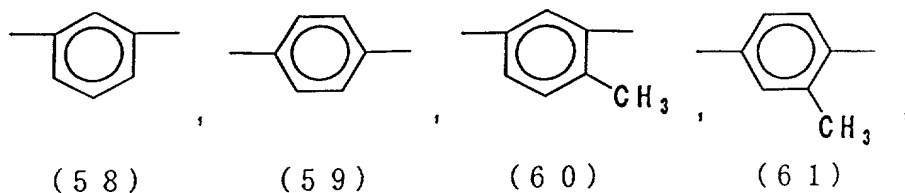
Liquid crystal alignment agent according to Claim 1 or Claim 2, where said polymer compound is polyurethane.

Claim 11.

Liquid crystal alignment agent according to Claim 10, where said polymer compound is polyurethane having the repeating unit comprising of the general formula (57) below



wherein R^{48} and R^{49} are independently of each other selected from radical shown in the formula (58) - (69) below



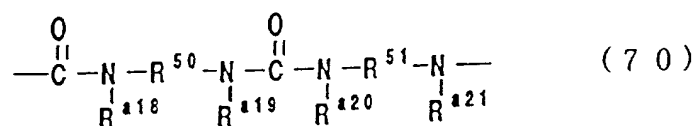
wherein R^{a16} and R^{a17} are independently of each other hydrogen, alkyl, substituted alkyl, aryl or propargyl.

Claim 12.

Liquid crystal alignment agent according to Claim 1 or Claim 2, where said polymer compound is polyurea.

Claim 13.

Liquid crystal alignment agent according to Claim 12, where said polymer compound is polyurea having the repeating unit of the general formula (70) below



wherein R⁵⁰ and R⁵¹ are independently of each other selected from formula (58) - (69) above;, and R^{a18} - R^{a21} are independently of each other hydrogen alkyl, substituted alkyl, aryl or propargyl.

Claim 14.

Liquid crystal device by the use of the liquid crystal alignment agent according to any one of Claim 1 through Claim 13.

Claim 15.

Alignment method of liquid crystals characterized by the use of the liquid crystal alignment agent according to any one of Claim 1 through Claim 13, where light or electron rays being irradiated over the thin polymer film formed on the surface of the substrate and achieving liquid crystal alignment without rubbing action.

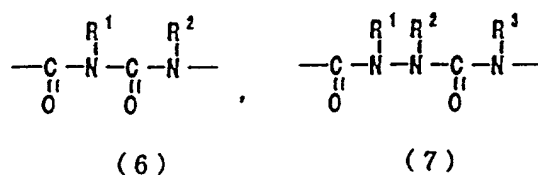
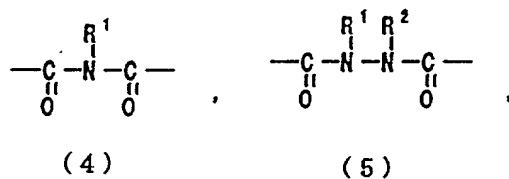
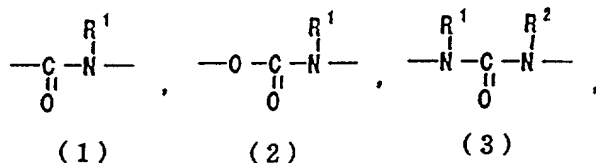
Abstract

Object

Liquid crystal-alignment agent where uniform liquid alignment of liquid crystals is effectively manifested by the irradiation with light over the liquid crystal alignment film without rubbing treatment of the liquid crystal alignment film thereof, and further manifests liquid crystal alignment with high stability and high light resistance, liquid crystals device with the use of said alignment agent and the method of the liquid crystal alignment by the use of said liquid crystal alignment agent.

Constitution

Liquid crystal alignment agent where polymer compound having bonds shown in the general formula (1) – (7) below



wherein R¹, R² and R³ are independently of each other hydrogen, alkyl,

substituted alkyl, aryl or propargyl; in the polymer compound thereof with number-average molecular weight of 1,000 – 300,000, and said bond makes the direct bond with either divalent or trivalent aromatic group at the both ends of said bond or with divalent or trivalent aromatic group making the direct bond at one end while at the other forming the direct bond with divalent or trivalent alicyclic hydrocarbon group, liquid crystal device by the use of said liquid crystal alignment agent and the method of the liquid crystal alignment by the use of said liquid crystal alignment agent.

**DECLARATION AND POWER OF ATTORNEY
UNDER 35 USC § 371(c)(4) FOR
PCT APPLICATION FOR UNITED STATES PATENT**

As a below named inventor, I hereby declare that:
my residence, post office address and citizenship are as stated below under my name;

I verily believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought, namely the invention entitled:

A LIQUID CRYSTAL ALIGNMENT AGENT AND LIQUID CRYSTAL DEVICE USING THE LIQUID
CRYSTAL ALIGNMENT AND METHOD FOR ALIGNMENT OF LIQUID CRYSTAL MOLECULES
described and claimed in international application number PCT/JP99/04575 filed on August 25, 1999

I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations §1.56.

Under Title 35, U.S. Code §119, the priority benefits of the following foreign application(s) filed by me or my legal representative or assigns within one year prior to my international application are hereby claimed:

Japanese Patent Application No. Hei 10-240491 filed on August 26, 1998

The following application(s) for patent or inventor's certificate on this invention were filed in countries foreign to the United States of America either (a) more than one year prior to my international application, or (b) before the filing date of the above-named foreign priority application(s)

I hereby appoint the following as my attorneys of record with full power of substitution and revocation to prosecute this application and to transact all business in the Patent Office:

S James A. Oliff, Reg.No.27,075; William P. Berridge, Reg.No.30,024;
Kirk M. Hudson, Reg.No.27,562; Thomas J. Pardini, Reg.No.30,411;
Edward P. Walker, Reg.No.31,450; Robert A. Miller, Reg.No.32,771;
Mario A. Costantino, Reg.No.33,565; and Stephen J. Roe, Reg.No.34,463.

ALL CORRESPONDENCE IN CONNECTION WITH THIS APPLICATION SHOULD BE SENT TO OLIFF & BERRIDGE, PLC, P.O. BOX 19928, ALEXANDRIA, VIRGINIA, 22320, TELEPHONE (703) 836-6400.

I hereby declare that I have reviewed and understand the contents of this Declaration, and that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

120	Typewritten Full Name of Sole or First Inventor	<u>Yukihiko</u>	<u>MIYAMA</u>
	Given Name	<u>Yukihiko Miyama</u>	Family Name
	Middle Initial		
**Inventor's Signature	<u>February</u>	<u>16</u>	<u>2001</u>
** Date of Signature	Month	Day	Year
Residence	<u>Funabashi-shi</u>	<u>Chiba</u>	<u>Japan</u> <i>JPX</i>
	City	State of Province	Country
Citizenship	<u>Japanese</u>		
	Post Office Address	<u>c/o Nissan Chemical Industries, Ltd. Central Research Institute, 722-1, Tsuboi-cho,</u>	
	(Insert complete mailing address, including country)	<u>Funabashi-shi, Chiba 274-8507, Japan</u>	

*Note to Inventor: Please sign name on line 2 exactly as it appears line 1 and insert the actual date of signing on line 3.

IF THERE IS MORE THAN ONE INVENTOR USE PAGE 2 AND PLACE AN "X" HERE ☒

PAGE 2 OF U.S.A. DECLARATION FORM
(Discard this page in a sole inventor application)

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Given Name Middle Initial Family Name

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*Date of Signature February 16 2001
Month Day Year

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**Inventor's Signature Hideyuki Endo

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Month Day Year

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Month Day Year

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address, including country)

Note to Inventor: Please sign name on line 2 exactly as it appears in line 1 and insert the actual date of signing on line 3.

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IF THERE IS FURTHER INVENTOR USE PAGE 3 AND PLACE AN "X" HERE ☒

PAGE 3 OF U.S.A. DECLARATION FORM
(Discard this page in a sole inventor application)

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of Fifth Joint

500 Inventor (if any) Yu NAGASE
Given Name Middle Initial Family Name

**Inventor's Signature [Signature]

*Date of Signature February 14 2001
Month Day Year

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600 Inventor (if any) Eiichi AKIYAMA
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**Inventor's Signature [Signature]

*Date of Signature February 14 2001
Month Day Year

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700 Inventor (if any) Nobukatsu NEMOTO
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address, including country)

Note to Inventor: Please sign name on line 2 exactly as it appears in line 1 and insert the actual date of signing on line 3.
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